Project Code :
(for RCMO use only)

UNIVERSITI SAINS MALAYSIA

RU GRANT FINAL REPORT FORM

Please email a softcopy of this report to rcmo@usm.my

A	**PROJECT DETAILS**
i	**Title of Research:** **OIL PALM BIOMASS ALKALINE PEROXIDE DIVERSIFIED PULP: MAPPING OF QUALITY TO APPLICATION BY DEGREE OF CHROMOPHORISATION**
ii	**Account Number: 1001/PTEKIND/814048**
iii	**Name of Research Leader: ARNIZA GHAZALI**
iv	**Name of Co-Researcher:** ▪ PROF. DR WAN ROSLI WAN DAUD ▪ ASSOC. PROF. DR BAHARIN AZHARI ▪ ASSOC. PROF. ISSAM AHMED ▪ DR RUSHDAN IBRAHIM (COLLABORATOR)
v	**Duration of this research:** **a) Start Date : 15 JANUARY 2009.** **b) Completion Date : 14 JANUARY 2012.** **c) Duration : 3 YEARS + 1 YEAR* EXTENSION.** **d) Revised Date** (*if any*) : 14 JANUARY 2013*.
B	**ABSTRACT OF RESEARCH**

(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English. This abstract will be included in the Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

English:

Treating the oil palm empty fruit bunches (OPEFB) with the alkaline peroxide witnessed a structural collapse, yielding fibrous materials with a portion of modified lignin and nano-scale ash remnants. Weak alkaline peroxide defiberated micro-fibrous pulp that suited paper making and packaging applications. By the synergy between extensive mechanical and chemical effects, various microfibrillar structures that partially split into nano-fibrils with diameters ranging from 10 nm to 100

nm were generated. On the pulp network, these nanofibrillar webs were responsible for the smoothing of the pulp network and this was done by masking of the physique of the individual microfibres. The masking effects, in turn, improved the printability of the ensuing paper and enhanced the value of the waste derivative. It is noteworthy that the production of the high quality fibre mass containing nanofibrillar web was only possible with ground EFB biomass in the 500 μm – 4 mm range due to auto-demineralisation arising from grinding and sieving. For a zero-waste process, the mass below 250 μm was converted into pollutant adsorbents and this points to a zero waste production of high quality nanofibrillar web production from oil palm biomass.

Bahasa Malaysia

Perawatan tandan kosong sawit (OPEFB) menggunakan peroksida beralkali menyaksikan keruntuhan struktur biojisim sehingga terbentuk sesawang fibril bersaiz nano yang masih terikat pada lignin terubahsuai dan abu pada skala nano. Dalam julat peratusan peroksida beralkali yang telah dikaji, peratusan kurang 10% menghasilkan gentian OPEFB bersaiz mikro yang sesuai dijadikan produk kertas dan bahan bungkusan. Dengan tindakan mekanikal dan bahan kimia pada tahap tinggi, terbentuk struktur fibril mikro yang terpisah separa kepada fibril dengan diameter dalam julat 10 nm hingga 100 nm. Kehadiran bahan berupa sesawang fibril nano tersebut berupaya meningkatkan kualiti percetakan laser ke atas kertas disebabkan kesan kelicinan daripada sesawang tersebut. Penekanan penting dalm penghasilan gentian bermutu tinggi berbentuk sesawang nanofibril ini ialah ia memerlukan EFB dalam julat ukuran 500 μm – 4 mm disebabkan sifat asas ternyah mineral yang berlaku secara spontan melalui proses penghasilan biojisim tersebut. Bagi menjadikan proses penghasilan sesawang nano yang sisa sifar, biojisim EFB berukuran kurang 250 μm digunakan sebagai penjerap bahan pencemaran setelah diubahsuai sifat kimianya. Dengan terbukti kebolehan menggunakan kesemua saiz biojisim EFB maka projek ini telah mendemonstrasi kaedah penghasilan sesawang fibril nano bermutu tinggi secara proses sisa sifar.

C BUDGET & EXPENDITURE

i

Total Approved Budget : RM 331981

<u>**Yearly Budget Distributed**</u>

Year 1 : **RM 150 527.00**

Year 2 : **RM 90 227.00**

Year 3 : **RM91 227.00**

Total Expenditure : RM331543.66

Balance : RM437.34

Percentage of Amount Spent (%) : 99.87%

-See Appendix 3 for e-statement.

Ii	**Equipment Purchased Under Vot 35000**

No.	Name of Equipment	Amount (RM)	Location	Status

 # Please attach the Asset/Inventory Return Form (Borang Penyerahan Aset/Inventori) – Appendix 1

D RESEARCH ACHIEVEMENTS

i Project Objectives *(as stated/approved in the project proposal)*

No.	Project Objectives	Achievement
1	Purify APP pulp	Pulp could be purified the same extent as chemical pulp ozone, peroxide and oxygen delignification but in different sequence. See student's thesis: Nurul Hasanah Kamaluddin **M. Sc. Thesis PPTI Universiti Sains Malaysia 2013.**
2	Produce CA film	CA production was possible even with alkaline peroxide pulp but the method is cumbersome and uneconomic. See **JIRCAS Working Report 73:178-182.**
3	Characterise dechromophorised EFB	Dechromophorised EFB collapsed as nanofibrils held/bound by modified lignin. See **Adv. Mat. Res. 832:500-505.** The wide variety of quality are described in **Adv. Mat. Res. 832: 487-493.**
4	Zero waste high quality fibre production and zero-cost** biomass processing	High quality fibre utilisation: See **Adv.Mat. Res.832:532-547.** Characterised the organism responsible for defiberation See & **Int. J. Scientific and Research Publication 4(4)**.**
5	Zero waste high fibre quality production system via waste utilisation.	2 means of waste utilisation was identified: 1- Via fines utilisation as paper filler See **Biores. 7(3):3425-3438** 2- The portion of particles undesirable for high quality fibre generation ($\leq$250 μm EFB particles as pollutant adsorbent.) performed well as pollutant adsorbent in acidic condition, which again points to the enhanced affinity of the biomass towards foreign materials upon modification of its lignobinding materials.See **Desalination and Water Treatment 2015, 1-14.**

Research Output

a) Publications in ISI Web of Science/Scopus

Publication (authors,title,journal,year,volume,pages,etc.)	Status of Publication (published/accepted)
1. Kamaluddin, N.H., Ghazali, A. and W.D. Wan Rosli (2012) *Potential of fines as reinforcing fibres in APP of OP EFB*. BioResources. (ISSN: 1930-2126), 7(3):3425-3438. Publisher: North Carolina State University (NCSU), 14 pages. (Impact Factor: 1.55)	Published
2. Ahmad, T. Rafatullah, M., Ghazali, A., Sulaiman, O., Hashim, R. and Ahmad, A. (2010*) Removal of Pesticides from Water and Wastewater by Different Adsorbents: A Review,* J. of Env. Sc. and Health, Part C: Env. Carcinogenesis & Ecotox. Reviews *28:231–271.*	Published
3. Dermawan, Y. M., Ghazali, A., Wanrosli, W. D. (2011) Effects of Multiple Impregnation on APP of EFB Cellulose Chemistry and Technology 45(5-6): 355-360.	Published
4. Danish, M., Ahmad, T., Hashim, R., Zukeri, M.R.H.M., Ghazali, A. and Sulaiman, O. *Characterization and Adsorption Kinetic Study of Surfactant Treated Oil Palm Empty Fruit Bunches* Desalination and Water Treatment (2015) Publisher: Taylor and Francis Group. (Impact factor: 0.99)	Published

b) Publications in Other Journals

No.	Publication (authors,title,journal,year,volume,pages,etc.)	Status of Publication (published/accepted)
1.	Ghazali, A., Ghazali, S., Zukeri, MRHM and Wanrosli, WD (2012). *Silica in EFB – An Infinite Amazement*. Malaysian Journal of Microscopy. (8): 70-74. Publisher: Universiti Putra Malaysia (UPM), 5 pages. (SCOPUS)	
2.	Dermawan, Y. M. and Ghazali, A. (2012). *Scanning electron microscopy for identification of paper strength development by two variations of refiner plate pattern* Malaysian Journal of Microscopy. (8): 65-69. Publisher: Universiti Putra Malaysia (UPM), 5 pages. (SCOPUS)	
3.	Ghazali, A., Kamaluddin NH, W.D. Wan Rosli and Rushdan I. (2012). *Sequential synergy of alkaline peroxide treatment and refining in co-generating filler for pulp web augmentation.* Iranica Journal of Energy and Environment, 3:6-13. Publisher: International Digital Organization for Scientific Information (IDOSI), 8 pages.	Published.
4.	Ghazali, A., Zukeri, MRHM, Dermawan, Y. M., Ghazali, S. and Wanrosli, WD (2014) *Nanofiber network rooted from the alkaline peroxide treatment of oil palm empty fruit bunches* Advanced Materials Research, 832:500-505, Publisher: Trans Tech Publications Inc., 6 pages. (SCOPUS)	
5.	Ghazali, A., Zukeri, MRHM, Dermawan, Y. M., Ghazali, S. and Wanrosli, WD (2014) *EFB nano fibrous cells for paper smoothing and improved printability* Advanced Materials Research, 832:537-542. Publisher: Trans Tech Publications Inc., 6 pages. (SCOPUS)	
6.	Ghazali, A., Zukeri, MRHM, Wanrosli, WD., Ahmed, T., Rushdan, I. and Ziya, A. K. (2014) *Augmentation of EFB fiber web by nano-scale fibrous elements* Advanced Materials Research, 832:494-499, Publisher: Trans Tech Publications Inc., 6 pages. (SCOPUS)	
7.	Dermawan, Y. M., Ghazali, A., Zukeri, MRHM, Kamaluddin, N. H. and Wanrosli, WD (2014) *Alkaline peroxide synergy with mechanical refining as factor in the development of EFB paper properties* Advanced Materials Research 832:487-493. Publisher: Trans Tech Publications Inc., 6 pages. (SCOPUS).	

11. Owolabi FAT*, Arniza Ghazali, Latiffah Zakaria and WD Wan Rosli (2014) *Pulpability of SAP Stained Elaise guineensis fronds for paper production* International Journal of Scientific and Research Publications 4(4): 12. Owolabi FAT; Arniza Ghazali and WD Wan Rosli (2014) *Diversified Biometric, Chemical and Morphological Composition of Elaeis Guineesis Frond Vascular Bundles for Pulp and Paper Configuration* IOSR Journal of Agriculture and Veterinary Science *7(4): 91-98* Publisher: International Organisation of Scientific Research, 9 pages	
13. Owolabi F.A.T., Ghazali, A., Wan Rosli, W.D. and Abbas F.M.A.K. (2015**) Oil Palm Fronds Responses to Alkaline Peroxide Treatment (Communicated). 14. Owolabi F.A.T., Ghazali, A., Wan Rosli, W.D. and Abbas F.M.A.K. (2015**) Influence of Treatment Duration and Chemical Level in the Alkaline Peroxide Pulping of Oil Palm Fronds (Communicated).	Under Review (Stated titles are temporary)

c) Other Publications
(book,chapters in book,monograph,magazine,etc.)

No.	Publication (authors,title,journal,year,volume,pages,etc.)	Status of Publication (published/accepted/ under review)

d) Conference Proceeding

No.	Conference (conference name,date,place)	Title of Abstract/Article	Level (International/National)
	Kamaluddin N.H., A. Ghazali, W.D. Wan Rosli and C.P.Leh (2012) JIRCAS Working Report, 73:178-182. Publisher: Japan International Research Center for Agricultural Sciences, 5 pages.	*Cellulose Acetates from the benign Alkaline Peroxide Pulping of EFB.*	International
	Khairil M.A.M.L, A. Ghazali and W.D. Wan Rosli (2012). JIRCAS Working Report, 73:166-171. Publisher: Japan International Research Center for Agricultural Sciences, 6 pages.	*Effects of alkaline peroxide percentages on the handsheets made from the alkaline peroxide pulp of EFB.*	
	Kamaluddin N.H., Ghazali, A. *, W.D. Wan Rosli,Ghazali, S. 2012. International Conference on Fundamental and Applied Sciences 2012 - American Institute of Physics Conference Proceedings 1482. Kuala Lumpur, pp.	*Changes in pulp web properties by addition of natural filler,*	International
	Kamaluddin N.H., Ghazali, A. *, W.D. Wan Rosli 2012. International Conference on Fundamental and Applied	*Characterisation of Mechanical Pulp Fines from APP of EFB*, Kuala Lumpur, pp.	International

			Sciences 2012 - American Institute of Physics Conference Proceedings 1482.		
			Dermawan Y.M., Ghazali, A. *, W.D. Wan Rosli, Khairil M.A.M.L 2012. International Conference on Fundamental and Applied Sciences 2012 - American Institute of Physics Conference Proceedings 1482., Kuala Lumpur, pp	*Alkaline peroxide pulping of oil palm empty fruit bunch by variation of chemical strength*	
			Zukeri, M. R. H. M.,A. Ghazali*,Khairil MAML 2012. International Conference on Fundamental and Applied Sciences 2012 - American Institute of Physics Conference Proceedings 1482. Kuala Lumpur.	*Morphological and mechanical effects of extended beating on EFB pulp web,*	International
			Ghazali, A. *, Kamaluddin N.H., C.P.Leh, W.D. Wan Rosli 2012. International Conference on Environmental Research and Technology (ICERT), Penang, Malaysia. pp.	*Augmentation Of Alkaline Peroxide Pulp Network By Co-Generated Filler*	International
			Dermawan Y.M., Ghazali, A. * 2012 International Conference on Environmental Research and Technology (ICERT)., Penang, Malaysia. pp.	*Surface morphology of papers from oil palm EFB alkaline peroxide pulp*	International
			Zukeri, M. R. H. M., Ghazali, A. *,Rushdan I.,W.D. Wan Rosli 2012. International Conference on Environmental Research and Technology (ICERT) Penang, Malaysia. pp.	*Trend in paper morphology and mechanical properties with extended beating of eb pulpmorphological and mechanical effects of extended beating on EFB,*	International
			Dermawan Y.M., Ghazali, A. *,Rushdan I.,W.D. Wan Rosli 2012. International Conference on Environmental Research and Technology (ICERT). Penang, Malaysia. pp.	*Identification of paper strength development by two variations of refiner plate pattern,*	International

 # Please attach a full copy of the publication/proceeding listed above (APPENDIX 4)

iii	**Other Research Ouput/Impact From This Project** *(patent, products, awards, copyright, external grant, networking, etc.)*

1. Appointment as Chair of Malaysian Standard development workgroup by Dept. Of Standards, Malaysia via SIRIM Berhad.
2. Malaysian Delegates to ISO TC 206 International Meeting in Bangkok, 2012
3. FRIM as collaborator.

E HUMAN CAPITAL DEVELOPMENT

a) Graduated Human Capital

Student	Nationality (No.)		Name
	National	International	
PhD	-	-	
MSc	2	1	1.Yunita Megasari Dermawan (International) 2.Nurul Hasanah Kamaluddin 3. Mohd Ridzuan Hafiz Mohd Zukeri
Undergraduate	Many	-	Nor Syazwani Nurul Ain Lew Chia Ying Haniza Abdul Rashid Muhammad Ilmi Izzuddin Jamaluddin Etc.

b) On-going (EXISTING) Human Capital

Student	Nationality (No.)		Name
	National	International	
PhD		NIGERIA	1. **ABDULWAHAB OWOLABI FOLAHAN TAIWO**
MSc	1	-	1.Muhammad Al-Amin Zaini (Reactivating candidacy December 2015)
Undergraduate		-	1. 2.

c) Others Human Capital

Student	Nationality (No.)		Name
	National	International	
Post Doctoral Fellow		1(INDIA)	1.Dr Tanweer Ahmad Khan
Research Officer	1		1.Mohd Ridzuan Hafiz Mohd Zukerl
Research Assistant	1		1.Mohd Azli Khairil Md LaziN

F	COMPREHENSIVE TECHNICAL REPORT
	Applicants are required to prepare a comprehensive technical report explaining the project. The following format should be used (this report must be attached separately): • Introduction • Objectives • Methods • Results & Discussion • Conclusion and Suggestion • Acknowledgements & References SEE APPENDIX 1

G	PROBLEMS/CONSTRAINTS/CHALLENGES IF ANY
	(Please provide issues arising from the project and how they were resolved) 1. Calibration of pulping equipment needs to be done periodically in order to reduce dependency on FRIM. 2. Fabricated refiners do not comply the standard pulping specification (corrosion resistant materials and coded blade pattern).
H	RECOMMENDATION
	(Please provide recommendations that can be used to improve the delivery of information, grant management, guidelines and policy, etc.) 1. Strict use of log book. Damage and malpractices in use of shared facilities such as PFI mill and Andritz refiner has to be penalised. 2. Close monitoring of machinery use by students should be mandated to the laboratory assistants in charge.

Project Leader's Signature:

....

Name : ARNIZA GHAZALI

Date : 6/11/2015

I	COMMENTS, IF ANY/ENDORSEMENT BY PTJ'S RESEARCH COMMITTEE

A few papers has been published in citation indexed journals.

Research constraints and recommendations stated are noted.

Signature and Stamp of Chairperson of PTJ's Evaluation Committee

Name : PROFESSOR DR. NORLI ISMAIL
Deputy Dean
(Research)
School of Industrial Technology
Universiti Sains Malaysia
11800 Penang Malaysia

Date : 14/11/15

Signature and Stamp of Dean/ Director of PTJ

Name : PROFESOR DR. AZHAR MAT EASA
Dekan
Pusat Pengajian Teknologi Industri
Universiti Sains Malaysia
11800 Pulau Pinang, Malaysia

Date : 12/11/15

UNIVERSITI SAINS MALAYSIA	# RU GRANT FINAL REPORT CHECKLIST

Please use this checklist to self-assess your report before submitting to RCMO.
Checklist should accompany the report.

NO.	ITEM	PLEASE CHECK (✓)		
		PI	JKPTJ	RCMO
1	Completed Final Report Form	✓	✓	
2	Project Financial Account Statement (e-Statement)	✓	✓	
3	Asset/Inventory Return Form *(Borang Penyerahan Aset/Inventori)*	✓	✓	
4	A copy of the publications/proceedings listed in Section D(ii) (Research Output)	✓	✓	
5	Comprehensive Technical Report	✓	✓	
6	Other supporting documents, if any	✓	✓	
7	Project Leader's Signature	✓	✓	
8	Endorsement of PTJ's Evaluation Committee	✓	✓	
9	Endorsement of Dean/ Director of PTJ's	✓	✓	

Appendix 1

UNIVERSITI SAINS MALAYSIA

BORANG PENYERAHAN ASET / INVENTORI

A. BUTIR PENYELIDIK

1. NAMA PENYELIDIK : ARNIZA GHAZALI
2. NO STAF : AA54548
3. PTJ : PUSAT PENGAJIAN TEKNOLOGI INDUSTRI
4. KOD PROJEK : 1001/PTEKIND/841048.
5. TARIKH TAMAT PENYELIDIKAN : 14 JANUARI 2013.

B. MAKLUMAT ASET / INVENTORI

BIL	KETERANGAN ASET	NO HARTA	NO. SIRI	HARGA (RM)

C. PERAKUAN PENYERAHAN

Saya dengan ini menyerahkan aset/ inventori seperti butiran B di atas kepada pihak Universiti:

TIADA PEMBELIAN DI BAWAH VOTE 35000
LIHAT APPENDIX 3.

....
(ARNIZA GHAZALI)

Tarikh: 6 NOVEMBER 2015.

D. PERAKUAN PENERIMAAN

Saya telah memeriksa dan menyemak setiap alatan dan didapati :

- ☐ Lengkap
- ☐ Rosak
- ☐ Hilang : Nyatakan..
- ☐ Lain-lain : Nyatakan ....

Diperakukan Oleh :

....

Tandatangan Pegawai Aset PTJ

Nama : ....

Tarikh : ....

***Nota :** Sesalinan borang yang telah lengkap perlulah dikemukakan kepada Unit Pengurusan Harta, Jabatan Bendahari dan Pejabat RCMO untuk tujuan rekod.

Oil Palm Biomass Alkaline Peroxide Diversified pulp: Mapping of Quality to Application by Degree of Dechromophorisation & Utilisation of Waste for Zero-waste Production System

Arniza Ghazali, Ph. D.
Principal Investigator
Research University (Individual) Grant 1001/PTEKIND/814048

Division of Bio-resource, Paper and Coatings Technology (BPC), School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia

arniza@usm.my

Keywords: Biomass, EFB, alkaline peroxide, oil palm, pulp, fibers.

Abstract. The increasing popularity of the oil palm empty fruit bunches (EFB) as a source of non-wood fibre has prompted a variety of research on processing and utilisation of the material. In an attempt to define the characters, reusability and end-of-life, oil palm EFB was processed by the alkaline peroxide variable treatment (APVT) systems. Low synergy between alkaline peroxide (AP) chemical and mechanical fibrillation through fibrillation (CMR synergy) revealed the yield of segments of EFB vascular bundles while heightening the mechanical forces further, generated more uniform but a mixture of fiber and segments of fibre bundles. An intermediate CMR synergy generated fibres forming a more well-defined but a rough resultant fibre network due to partial fibrillation of the vascular bundle. Applying maximal CMR synergy was found to generate higher yield of network strengthening fibrous cells. These were later identified as nano-scale fiber network or "nano-scan", consisting of 10-80 nm diameter fibers arranging themselves in a systematic network. Analysis of the polarity of fibers harvested from the APVT systems manifests the systematic construction of nano-fibrils winding in helical manner to form arrays of nano-fibres that glue themselves together as micro-fibrils. Interconnections between fibers and other gluing elements led to the vascular bundle known as the EFB biomass that was once dross and that can now be marvelled as an alternative source of nano-fibers for the nano-industry sector.

Introduction

Famed for strength factor of botanical structures [1], the abundant, renewable and biodegradable cellulose [2] fibers have long been recognised for their vast list of applications. While micro-fibers serve the common functions in the making of pulp-based products, nano-fibers define a new edge of fiber utilization. Driven by such key areas as electronics, energy, medicine, chemicals, coatings, catalysis [3] as well as textile and apparel [4], today, nano-fibers find dominant use in the mechanical and chemical industry, which accounts for more than half of the total market share [5]. The big impact of this sector is implied by a ten-fold increase in the production of nano-fibers in 2011, in comparison to that reported in 2002. Projecting an extended end-user market, the production volume in 2016 is conservatively estimated to reach more than 350 000 tonnes, with nano-cellulose and nano-fibres included in the tonnage [3]. The enormous growth is due to their unique properties such as large specific surface area, small pore size, high porosity and a smaller diameter size over the conventional fibers [5].

The expanding demand for nano-fiber and nano-cellulose prompts the need for an efficient nano-fiber production line with flavours of flexibility, cost effectiveness, speed and environmental compatibility. This is essential in ensuring an extra long-term sustainability of the supply regime. In line with this, the potential of the abundant residual materials such as the oil palm biomass for application in this sector is worth a study. Being one of the influential sectors to global GDP [6], the as a wealth factor for the packaging industry. By switching from wood-based imported fibers to the use of EFB as source of fibers, for instance, a 63% saving on the capital for raw materials was proven achievable [7]. Beyond packaging works that has saluted EFB as profit-making item, high-end uses of the materials are also projectable in the advent of nano-technology infused with the idea of renewability and sustainability.

Commensurate with this, a study focusing on the fibrous contruction of the said popular local biomass was carried out. Beyond the conventional fibre, an eco-friendly [8] fibre extracting agent called the alkaline peroxide is used to liberate the finest possible nano-fibers. As fascinating fibers and cells could be obtained by adaptation to the various possibilities of alkaline peroxide chemical level and mechanical fibrillation [9-12] synergy, the system adopted for studying the ultra-structure of fibrous materials is denoted as an alkaline peroxide variable treatment or APVT system. This paper discusses the pathway for liberating and understanding the nano-fiber contrstruction in the EFB biomass.

Methodology

Processing of Oil Palm Biomass. The fibrous strands of EFB in the form of the dried long fibrous strands or vascular bundles were washed and air-dried indoor. A portion of these were ground to 500 □m particles while the rest were downsized to 2 cm segments.

For oil palm fronds, 3 cm x 3 cm chips were produced by segmentation of the rachis. These were then hammered to obtain a loose form of vascular bundles.

For both EFB and OPF, measures of removing the non-cellulosic materials were taken as a biomass pre-treatment process. Soaking the biomass in distilled water for 30 to 40 minutes at 70°C could remove 50% of the extractives materials. Gentle splitting of the vascular bundles into thinner strips was achieved by pressing the materials at 15 psi.

Tracking Delamination and Fibrillation of EFB. In this paper fibrillation is used to refer to the process of generating fibrils while delamination refers to the peeling out of the thin layer of nano-fibril web (TN-webs) or nano-scale elements (nano-scan) from the fiber or micro-fibril. It was identified that the synergy between the alkaline peroxide chemical and mechanical refining, AMR, which is also abbreviated as CMR for chemical-mechanical refining, can be synergised differently to initiate different extents of fibrillation. In an alkaline peroxide various treatment (APVT) system, the basic CMR synergy is referred to as an APMP system and a wide variation in refining mode was also attempted [9-12]. Table 1 provides the summary of CMR synergy in the adopted APVT system.

Table 1: Speciation of the APVT Systems

System vs CMR Synergy	Alkaline Peroxide Impregnation, API (AP Level and Stages)			Mechanical Refining		
				M1 10-60 kWh/t	M2 10-60 kWh/t	M3 12-80 kWh/t
	2:2.5%	4:5%	8:10%			
Low CMR APMP	■			■		
High CMR APP	■■	■■	■■		■■	
APFI		■			■	■

NB: ■ Single alkaline peroxide impregnation (1-API) | ■■ Multiple-stage API

Fiber extraction via APVT systems were carried out on the cleaned and segmented or particle form of EFB. To observe segmented vascular bundles, APMP was carried out, which involved only low energy refining of the AP-treated EFB. By employing the most severe condition (APFI), diversified fibrous cells could be obtained and these were classified accordingly and stored for analysis.

Microscopy Analysis. Light microscope model Olympus BX41 was used to analyse isolated fibers on a slide of thin smears of fibers. These were then observed under Leo Supra, 50 VP, Carl Zeiss Scanning Electron Micrograph. The samples were placed on a stub using double-sided electrically conducting carbon adhesive tapes and then gold coated using Polaron Equipment Limited model E500 with a voltage of 1.2kV and 20 Pa for 10 minutes. EDAX was run to arrive at semi-quantitative results.

Results and Discussion

Oil palm empty fruit bunch vascular bundles (EFB), a monocot famed as *Elaise guineensis* amongst botanical scientists, is at origin brownish, attributable to the 5% redness, 19% yellowness and 20% vividness [12]. To naked eyes, the soft brown tone of the biomass imparts 64% lightness on CIELAB chromaticity scale, which corresponds to 13% ISO brightness [12]. From chemistry viewpoint, the colour factor of EFB is governed by the chromophoric materials from the extractives, lignin and transition metals. Upon reaction with alkaline peroxide, chromophoric groups are altered somewhat and a portion of these are released as auxochromic materials while a portion is retained as light lignin fragments (LLF). Despite retention of LLF, it is noteworthy that fiber webs derived from the APVT systems offer good photostability [13] with pleasant dose of eye-relaxing yellow tone.

The alkaline peroxide effects aided in the liberation of fibers. Theoretically, this occurred as a result of lignin modification and hence, lowering the capacity of the binding materials [14, 15]. Physically, the swelling and softening of EFB lubricated shearing of the vascular bundles, freeing fibrous mass of varying shapes and sizes. The thoroughness of this process is therefore decided by the extent of the alkaline peroxide chemical (C) penetration (and reaction with lignin as the principal non-cellulosic components of EFB), which could not be separated from the mechanical refining (MR) process. Whether alkaline peroxide is present as residue or as fresh chemical, the CMR synergy is the key factor not only in liberating fiber but in attaining the target fiber morphology.

Beginning with the lowest-end of the APVT system, Fig. 1 presents the fibrous mass as blend of vascular bundle segments, fibre bundles and less of individual fibers. The poor alkaline peroxide reaction with EFB is apparent from the presence of intact silica and silica craters on the biomass structure as elsewhere [11] described. The presence of these segments amidst single fibres and fibre bundles resulted in low paper strength and coarse paper network (Fig. 1a) due to the non-uniformity of the fibre web structure. The low fiber network strength is also attributable to the interruption of fiber-to-fiber bonding. Evidence of segmented vessel elements (circle in Fig 1a) is an important factor to the poor inter-fiber bonding, particularly if located within the web cross-section structure. This is shown in isolation in Fig. 2 with vessel element encountered in the APMP system manifesting the typically segmented structure of monocots [11].

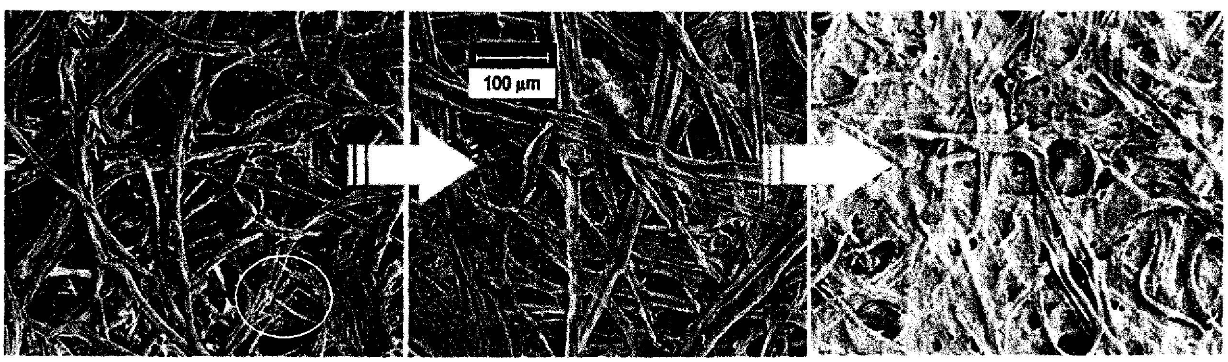
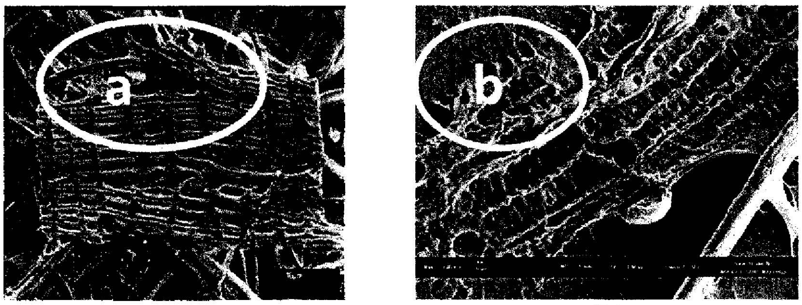


Fig. 1: Transition in thoroughness of EFB fibrillation via APVT system (a) APMP (b) APP (c) APFI.

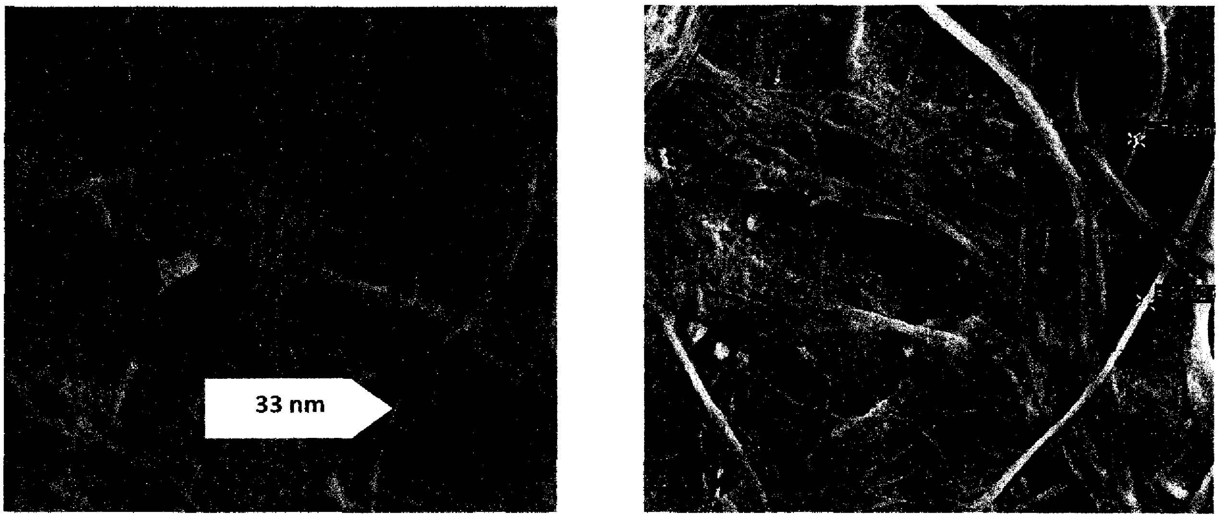
Quite directly inferable is the fact that raising the level of alkaline peroxide would result in an ease of further fibrillation of the fibre bundles to yield more of the single fibres. The latter effects were particularly favourable in giving strength as well as aesthetic and kinaesthetic values to the fibre network (Fig. 1c), as a result of extensive fibrillation arising from the effective CMR synergy. The segmented vessel element from the APMP system (Fig. 2a) seemed delaminated into a layer of pitted structure (Fig. 2b) as a result of heightening the AP level and repeating the alkaline peroxide impregnation stages in the APP system. In fact, more evidence of delamination could be claimed from an APP system as compared to the APMP system, implied by the relatively higher abundance of cell delamination.



(a) (b)

Fig. 2: Splitting and delamination of EFB vessel elements (a) segmented vessel on fiber web (b) layer of delaminated vessel structure.

It is also important to note that fibre strips (Fig. 1c) are less apparent due to the presence of the masking cell layers. This is attributable to the more extensive delamination effects as in Fig. 2b, which also resulted in the layering and masking of paper surface as in Fig. 1c. A close-up look at similar structures shown in Fig. 3a, indeed, demonstrates that the masking layers are constructed by arrays of nano-fibrils with the underlying layer showing systematic arrangement and those atop are more randomly placed. Also evident from Fig. 3b are the individual nano-fibrils of variable diameters, typical of micro-fibrillated cellulose [16]. For ranging between 1 nm to 100 nm diameter, by standard definition [17], these are classifiable as nano-fibers.



(a) (b)

3: Thin nano-fibril web (TN-webs) that are magnified to estimate and view nano-fibrils

Delamination Check. CMR synergy is easier to imagine by correlating the fibrillation effects to the fibre sizes. Table 2 matches the fiber sizes with the possible different CMR effects, with each tick representing proof of observation. Related observations are presented in Fig. 4.

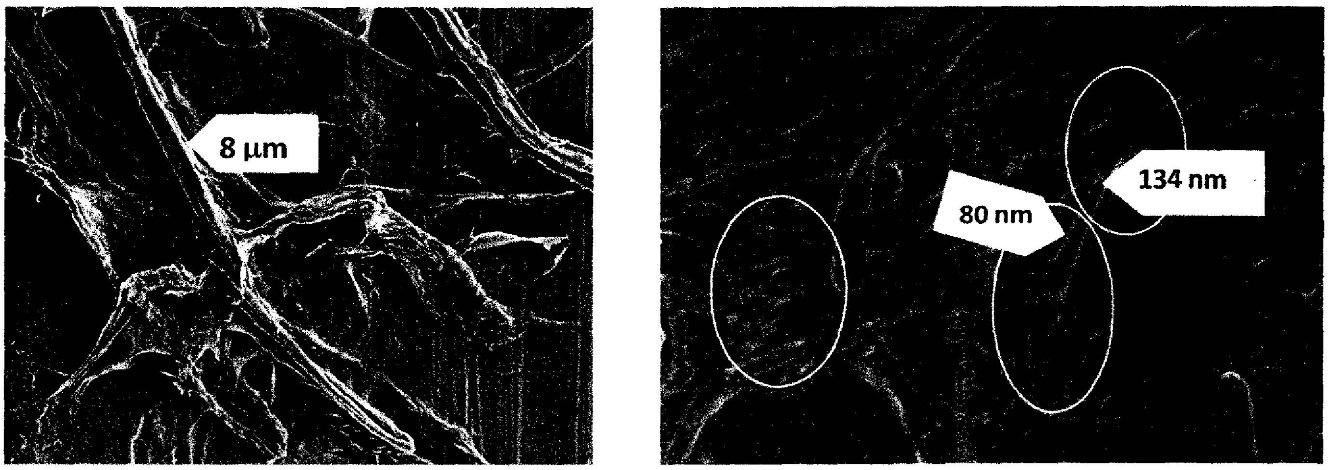
Table 2: Extent of Shearing Effects

Structure &Dimension	Mechanical Refining Effects		
	Fibrillation	**Delamination**	**Condition**
Vessel Element and vascular bundle			APMP
Macro-Fiber (>500 μm)	✓	✓	APP
Micro-Fibril			
5-100 μm	✓	✓	APFI;APP
<1 μm	✓	✓	APFI; APP
Nano-fibril			
80-100 nm		✓	APFI
< 80 nm	✓	ND	APFI

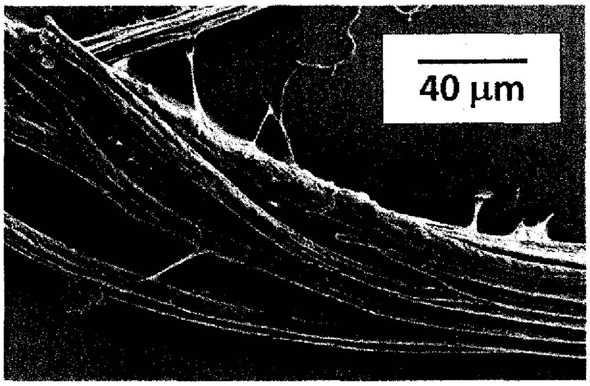
NB: segmentation, split and kink are common phenomena.

Macro-fibres: diameter about 1 mm | micro-fiber (EFB[18]): diameter≡8-26 □m | Fibril≡ >8□□m

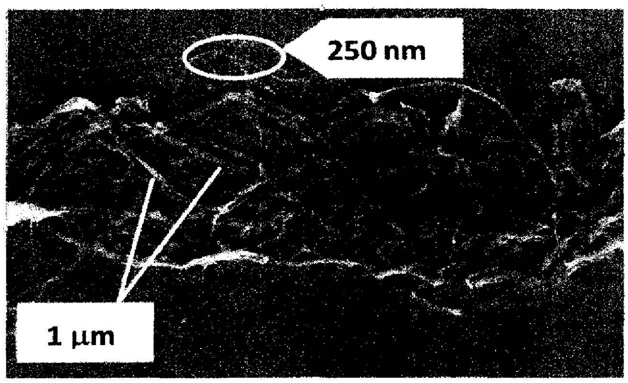
Nano-fibril≡1-100 nm [16],[17].



(a) (b)



(c)



(d)

4: Delamination effects (a) of 8 µm (diameter) fiber (b)10-134 nm fibril (c) of 25 µm fibre fibrillated from the 40 □m split vascular bundle forming (d) checkerboard pattern attributable to helical winding of EFB micro-fibrils.

Fig. 4 presents the extents of delamination effects amongst fibers rooted from EFB via APP and APFI systems. Extensive delamination was achievable by multi-stage API and refining denotable as high CMR synergy (Table 1) in the APP system. The resultant structures classified as EFB fiber [18] having diameter of 8 µm (Fig. 4a) must have arisen from the peeling of TN-webs initially wound to form a larger diameter fiber. Fibers fibrillating from the 40 □m split vascular bundle, however, is also associated with APP systems, indicating partial uniformity of fibre sizes derived from the system. An extended CMR synergy offer fibrillation of the 134 nm fibril (Fig. 4b) and these are magnification of TN-webs that are more extensively delaminated fiber or the less extensively layered structure incomparison to the more intact fibrous mass in Fig. 4d. Multiple layer of the undelaminated or more bound layered structure of fibre webs results in the checkerboard pattern in Fig. 4d and this is another proof of systematic helical winding of fibrils around EFB micro-fibrils. The fact that these are still bound to the parent fibril and bound to each other as a web, indicates an incomplete removal of the recalcitrant binding materials such as modified lignin (LLF) and the skeletal silica, which, like cellulose, is also the structural strength factor to EFB.

Thus far, generation of the thin layer of nano-fibrils, was seen as occurring on several scales of fibrillar cells, depending on the applied fibrillation energies. Governed substantially by CMR synergy, the onset of delamination of the micro-fibers was detected in the APP system. This suggests that delamination is favoured by application of multiples of 10 kWh/t to 60 kWh/t refining energy and a multi-stage alkaline peroxide impregnation stages to attain significant amount of nano-fibril webs. At x5000 magnification of the TN-webs (Fig. 4b), several of the 134 nm fibril were detected as splitting into at least 11 fibrils, suggesting a 12 nm range fibrils dangling to a parent fibre. The diminution in the fibril diameter indicates a strong possibility of generating long nano-fibers under a more gentle subsequent mechanical fibrillation but additional dose of alkaline peroxide to act upon the non-cellulosic component responsible in hinging complete liberation of the nano-fibrils. The challenge of incomplete nano-fibrillation was also encountered in established oxidative procedures such as TEMPO-assisted techniques [19-23]. In the case of CMR synergy, subsequent reactions of these nano-fibrillar mass with a carefully controlled CMR synergy is projected to liberate individual nano-fibers from the TN-webs, which are also interchangeably addressed as nano-scan.

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At the present stage of knowledge, the presence of TN-webs in the fibre network was able to boost tensile strength by several folds. In comparison to the fibre network from the APMP system, APFI system offered 900% improvement in the strength of fiber network. This signifies the optimism for EFB as a renewable source of nano-fiber for development of future super-strong fiber-based products. In light of rapidity and relative eco-friendliness [12] of the APVT system, the discussed method has in intrinsic ways laid a promise for a competent and sustainable way of cascading nano-fibril network from EFB biomass. Subsequent CMR synergy that could remove such fibre-cementing materials as residual lignin as the aforementioned light lignin fragments, LLF, and skeletal silica shed the light for nano-fibre production from EFB via alkaline peroxide pathway.

SUMMARY

The degree of dechromophorisation by alkaline peroxide action towards the oil palm empty fruit bunches (EFB) was studied based on the prior knowledge that alkaline peroxide attacks the lignin components of biomass. The principal marker of dechromophorisation, on the other hand, is the degree of fibrillation and the sites at which fibrillation occurs. This occurs as shearing forces affect the weaker region of the biomass more than the parts that had least reacted with the lignin-modifying chemical. With an increase in the chemical and mechanical synergy (55 KWh/mt for basic APMP to $15x10^3$ KWh/mt for APFI system), fibrillation of EFB was enhanced. Having established the relationship that lignin modification points are the weaker and are the potential fibrillation sites, fibrillation characters are therefore the marker of dechromoporised sites. The related applications of the produced fibers and the interactions between the various phases of the findings can be summarised and portrayed in Fig. 1.

From an APMP system applying below 10% alkaline peroxide, pulp of lower quality with a mix of macro and micro-fibres were obtained. Owing the non-uniformity of sizes and colours attributable to the uneven extents of EFB-AP reactions, the fibrous mass only suits moulded pulp application such as production of meal boxes, electronic trays and other cushioning applications. Increasing the level of AP beyond 10% allows production of more uniform micro-fibres. These are more suitably used as packaging papers such as wrappers as they are less coarse than APMP pulps. Improving the synergy between AP and mechanical fibrillation improved the inter-fibre bonding further. With extreme mechanical energies, nanofibrillation occurred intensively, giving the fibre network a fine, smooth and translucent appearance. Besides improvement in printability, this also suits interior decoration. Use as eco and halal food packages are also a possibility as these are free of hazardous chemicals and 100% botanical fibres. The found favourable effects of nano fibre web on printability has defined one application of nanotechnology in the papermaking from EFB as a local biomass.

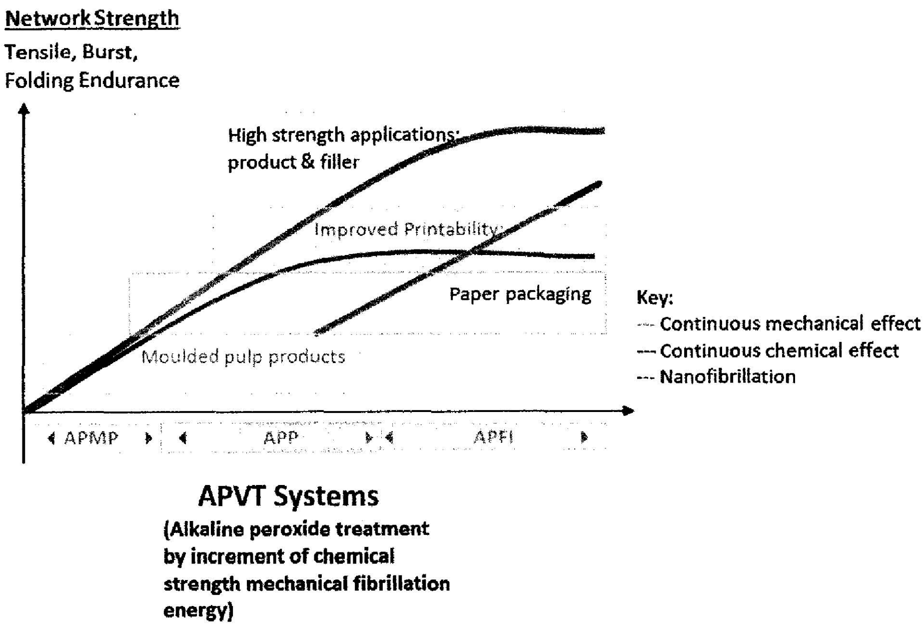

Fig. 1: EFB fibre network strength versus applications and systems strength.

Conclusion

- Fibrillation of TN-webs was made possible by the reaction between alkaline peroxide with the chromophoric materials that also participate in the gluing of fibrils into webs. This facilitated the liberation of the thin layer nano-webs (TN-webs).
- APFI and APP are APVT systems that are capable of generating thin nano-fibril webs (TN-webs) from EFB.
- Evidence of helical winding of nano-fibrils around fibers and submicron fibrils explains the net feature of TN-webs. This also demonstrates the position of the binding materials that should be attacked for cascading nano-fibers from EFB.

Acknowledgement

This work was funded by Ministry of Science, Technology and Innovation (MOSTI) through Research University grant 1001/PTEKIND/814048. Students working on this project received NSF scholarship, USM Fellowship, Graduate Assistantship and PRGS grant 1001/PTEKIND/832013 from Universiti Sains Malaysia.

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ANNEXES: ZERO-WASTE SYSTEM DEVELOPEMENT FOR EFB NANOFIBRILLAR WEB PRODUCTION

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Taylor & Francis

Characterization and adsorption kinetic study of surfactant treated oil palm (*Elaeis guineensis*) empty fruit bunches

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ABSTRACT

Oil palm (*Elaeis guineensis*) empty fruit bunches (OPEFB) was treated with cetyltrimethylammonium bromide (CTAB) to make its surface suitable for methyl orange (MO) dye adsorption. CTAB-treated OPEFB samples were characterized for their surface functional groups using FTIR, pHzpc, proton-binding capacity, and Boehm titration techniques. The surface morphology and elemental composition of the sample were also studied, employing field emission scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS). It was found that in totality, acidic surface functional group increased after CTAB treatment. The adsorption process was well explained with pseudo-second-order kinetic model. The obtained equilibrium sorption data were then analyzed using the Langmuir, Freundlich, Dubinin–Radushkevich, and Tempkin isotherms. The results showed that sorption was surfactant dose dependent and adsorption increased with an increase in the percentage of surfactant applied on the OPEFB. The maximum adsorption of MO was found at 1% surfactant treatment dose. It was also determined that MO adsorption onto the OPEFB treated with 1% CTAB solution (1% CTAB-OPEFB) followed the monolayer (Langmuir) adsorption. The maximum adsorption capacity of 1% CTAB-OPEFB for the removal of MO was found to be 18.08 mg/g at 298 K (at pH 6.3). Thermodynamic study revealed that the adsorption process was spontaneous and exothermic in nature. There was no energy barrier to initiate the adsorption of MO dye on the CTAB-treated OPFB.

Keywords: Adsorption; Isotherm; Methyl orange; Oil palm empty bunches; Surfactant; Cetyltrimethylammonium bromide

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		$(mg/g/min^{1/2})$
Q	—	proton-binding capacity (mmol/g)
V_0	—	volume of background electrolyte (mL)
V_t	—	volume of the titrant (0.1 M NaOH or 0.1 M HCl) (mL)
m	—	mass of the adsorbent (g)
$[H]_i$	—	initial hydronium ion concentration (mol/L)
$[OH]_i$	—	initial hydroxyl ion concentration (mol/L)
$[H]_e$	—	hydronium ion concentration at equilibrium

APPENDIX 3

Year: 2013

Budget Account Code	Roll over	Commit	Actual	Available	Percentage
1001.111.0.PTEKIND.814048	37,362.56	0.00	0.00	37,362.56	0.00%
1001.114.0.PTEKIND.814048	-242.16	0.00	0.00	-242.16	0.00%
1001.115.0.PTEKIND.814048	-560.00	0.00	0.00	-560.00	0.00%
	36,560.40	0.00	0.00	36,560.40	0.00%
1001.221.0.PTEKIND.814048	-843.30	0.00	0.00	-843.30	0.00%
1001.222.0.PTEKIND.814048	-150.00	0.00	0.00	-150.00	0.00%
1001.223.0.PTEKIND.814048	1,469.88	0.00	0.00	1,469.88	0.00%
1001.226.0.PTEKIND.814048	-2,886.00	0.00	0.00	-2,886.00	0.00%
1001.227.0.PTEKIND.814048	-57,984.34	3,580.35	0.00	-61,564.69	0.00%
1001.228.0.PTEKIND.814048	2,643.00	0.00	0.00	2,643.00	0.00%
1001.229.0.PTEKIND.814048	-6,521.98	1,515.00	0.00	-8,036.98	0.00%
	-64,272.74	5,095.35	0.00	-69,368.09	0.00%
1001.335.0.PTEKIND.814048	33,300.00	0.00	0.00	33,300.00	0.00%
	33,300.00	0.00	0.00	33,300.00	0.00%
1001.552.0.PTEKIND.814048	-54.97	0.00	0.00	-54.97	0.00%
	-54.97	0.00	0.00	-54.97	0.00%
	5,532.69	5,095.35	0.00	437.34	0.00%

Financial Expenditure

Amount of Grant Approved	:	RM33 1981
Cumulative Disbursement	:	
Balance of Allocation (not received yet)	:	RM437.34

No.	Items	Approved Grant	Expenditure to date		
			Actual spending	Available 2013	Commitment
1.	Temporary and Contract Personnel (V11000)	101 181	63 818.44	37362.56	*
2.	Travel and subsistence (V21000)	11 000	11242.16*	-242.16	
	Transportation (V22000) – to Balik Pulau for OPF	0	560.00	-560.00	
3.	Communication & Utilities (V23000)	500.00	30.xx	1469.88	
	Rental (V24000)	0	-	-	
	Raw Materials, Repair, Maintenance (V26000)	0	2886.00	-2886.00	
4.	**Research Materials and Supplies (V27000)**	140 000	**201 564.69**	-61564.69	
5.	Minor Modifications and Repairs (V28000)	4 500	1857	2643.00	
6.	Special Services (V29000) – LM/SEM/NMR/IR/AAS **Analyses, Honorarium, Conferences, Workshop-Training.**	27 000	**35 036.98**	-8036.98	437.34
7.	Special Equipment and Accessories (V35000)	46 800	13 800	33 300.00	
<u>Notes:</u>	**TOTAL (RM)**	**331 981**	331 543.66	**437.34**	

POTENTIAL OF FINES AS REINFORCING FIBRES IN ALKALINE PEROXIDE PULP OF OIL PALM EMPTY FRUIT BUNCH

Nurul H. Kamaludin, Arniza Ghazali,* and Wanrosli Wan Daud

Pulp from the alkaline peroxide mechanical pulping (APMP) of oil palm empty fruit bunch, EFB, was fractionated with varying mesh-size screens to examine the effects imposed by size-specific fines on the produced pulp network. Occurring mainly as a result of refining, fines elements with dimensions almost resembling EFB fibres were the long tube-like tapered vessels from the arrays of adjoined cell walls detached along the perforation lines. These fibrillated vessel elements constituting the P250/R300 fines fraction improved pulp network strength by gluing onto multiple fibres. More profound strength enhancement was promoted by the segments of the fibrillated vessel elements constituted in the P300/R400 fines fraction. With reduced dimensions, these elements enhanced pulp network strength by filling the micro-voids in the pulp network. By eliminating gaps that would otherwise interrupt inter-fiber bonding, 12% P300/R400 fines fraction enhanced the EFB APMP pulp network tensile strength by 100%.

Keywords: APMP; EFB; Fines; Filler; Reinforcing; Vessel elements; Fibrillar

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INTRODUCTION

Global resources consumption for 2010 reveals a persistent dependency on wood as a natural resource for pulping and papermaking, and this intensifies concerns over world carbon emission from deforestation. To gradually reduce the 70%-to-30% portion of wood-to-nonwood fibre supply, pulp and paper consumption patterns need to be revisited (Madakadze *et al.* 2010). Adaptation of existing technology and innovation of technology for pulping and processing of non-woody materials, which can be extra demanding in comparison to wood pulping (Rousu and Niniimaki 2005), also needs extensive research and proper documentation. Renewed interest in non-wood utilization research activities need proper monitoring and redirecting to ensure adherence to sustainability strategies such as cradle-to-cradle and cradle-to-gate product life cycle, as well as zero-waste systems. These efforts point to waste minimisation and benign carbon accounting results.

Asia is an influential source of non-wood pulp from annual fiber crops, agricultural residue (or agro-waste), and non-plant fibrous mass such as algae, rags, and animal waste. In the course of palm oil milling in Malaysia, for instance, 19.3 million tonnes of EFB is generated each year as the palms are pruned for oil extraction (Hoggard 2011). Traditionally, the EFB are left to rot in the environment or burnt in open air, which creates tremendous environmental concern. While open burning pumps in carbon dioxide

into the atmosphere (an excess of which can lead to global warming), leaving the residual fruit bunch to rot in the environment attracts pests, besides being a source of foul odour. Utilisation of the industrial-cum-agricultural residue, therefore, offers productive management of the waste from the country's major cash crop. From a pulp productivity perspective, per hectare palm oil plantation could generate EFB pulp at least double the per annum pulp harvested from the local rainforest. This corresponds to savings of an equivalent of over 88 million trees, on the assumption that all EFB could be converted to pulp (Hoggard 2011).

To date, research on utilization of EFB continues to grow. EFB can be minimally processed to suit application as pollutant sorbents (Ahmad *et al.* 2010, 2011a,b). It is also a type of biomass currently researched for the practical possibility of biofuel production, despite the often-said snags. Beyond research, today a small amount of EFB is used as medium-density fibreboard, mats, mattresses, cushions, and for light furniture. It is also compressed as briquettes and incinerated for electricity generation (Hoggard 2011). Similarly, destruction of EFB lignocellulose matrix allows production of melt siliceous glaze by high temperature incineration of the biomass. This has enticed creative application such as glazing of ceramics and pottery (Ghazali *et al.* 2009), for interior decoration application. In a contrasting application, as EFB has a predominance of cellulose, has lower lignin in comparison to most local wood, and has unique fibre characteristics, the residue has greater viability as raw material for pulping and conversion to paper-based products (Ghazali *et al.* 2006; Zainon 2011; Anon 2011) as compared to bioenergy (Anon. 2011) and glazing applications.

Pulp extraction from EFB was therefore attempted by applying an environmentally benign (Ghazali *et al.* 2009) process concept of the alkaline peroxide mechanical pulping, APMP. Being sulfur- and chlorine-free, the technique incorporates pulping and bleaching in a single process, thus eliminating the need for a separate bleach plant and the ensuing operation and maintenance costs. Apart from the acclaimed (Xu, 1999, 1999a; 2000b; Bukhart *et al.* 2001; Xu 2001a, 2001b, 2001c) simplicity, various possible adjustments can be made to the refining parameters, alkaline peroxide level, stages, and temperature of the alkaline peroxide to suit the choice of biomass and the resultant pulp quality. The process flexibility and high adaptability to a wide spectrum of biomass was first demonstrated by Cort and Bohn (1991) based on the success of APMP™ of wood species such as aspen. Subsequent works reported successful application of the system to birch, maple, and poplar (Blodgett *et al.* 1997; Francis *et al.* 2001). Through certain upgrading measures, Xu and co-workers reported success of adapting a modified APMP system (Xu 1999) to kenaf, straw, baggase, and jute (Xu, 2001a,b,c), as well as to selected tropical hardwood such as acacia mangium (Xu, 2000b).

Early attempts of adapting APMP to EFB (Ghazali *et al.* 2006, 2009; Muhd Yusof *et al.* 2010) observed the wide possibility of pulp quality by adjustments of experimental parameter and machinery. The usefulness of fines co-generated by the mimicked APMP system (hereby denoted APP for alkaline peroxide pulping) was also observed (Ghazali *et al.* 2011), in contrast to the undesirable effects of wood fines and short fiber (Colley 1973) reported previously. Usefulness of wood and non-wood market pulp fines is in wider literature coverage (Gorres *et al.* 1996; Sundberg *et al.* 2003; Rousu and Niinimaki 2005; Chevalier-Billiosta *et al.* 2007; Subramanian *et al.* 2008; Dooley and Weinberg

2009; Asikainen *et al.* 2011). Lukko and Paulapuro (1999) found that desirable fines were generated with intensified refining. While flakes were found to be of less value (Luukko and Paulapuro 1999; Subramanian *et al.* 2008), fibrillar structures were found to render paper density, less of solid-air extension and therefore improved optical qualities. Early attempts of APP of EFB not only showed encouraging effects of fines on paper strength (Ghazali *et al.* 2011) but also 70% improvement in refining discharge clarity, which is important in reduction of total suspended solids (TSS) in used process water. At the present level of knowledge, TSS reduction is achieved by backwash filtration technology, adopted in the whitewater closed-loop systems where reuse of water in the water-intensive industry is made more efficient (Shukla *et al.* 2012). This paper presents the types of fines elements in EFB APP pulp and identifies the strength-reinforcing potential of the pulping by-products. As EFB pulp is gaining worldwide acceptance as blended pulp in many industrial paper and packaging products, knowledge of the characteristics and potential uses of the waste material is especially important in maximization of process yield and minimization of waste.

EXPERIMENTAL

Materials

The fibrous strands of EFB were obtained from Sabutek (Malaysia) Sdn Bhd in bales of dried long fibrous strands. These consisted of vascular bundles that were washed and air-dried upon receipt and the strands were then cut into 2±0.5 cm segments at Universiti Sains Malaysia (USM) laboratory.

Methods

Pulp preparation

APMP of EFB was carried out by simplification of the previously adopted method (Ghazali 2006). On a partially extractive-free EFB segments that were obtained by soaking the biomass in distilled water at 70°C for 30 minutes in water bath, 15 psi or 103 kPa pressure was applied on the decanted EFB using an impregnation device. Upon release of pressure, the alkaline peroxide chemicals were allowed to impregnate into the biomass at a consistency of 10-to-1 liquor to EFB ratio. The alkaline peroxide containing 2% sodium hydroxide (NaOH) and 2.5% hydrogen peroxide (H_2O_2) was reacted with EFB, and this cooking process was allowed for 30 minutes to soften and brighten the biomass. This was again pressed at 15 or 103 kPa until reaching a dewatering rate of three drops per minute. The EFB was next refined using Sprout-Bauer 12" single disc refiner with resultant specific refining energy of 54.95 kWh/t for 4% pulp consistency and refining temperature of 33.5°C

Fines Collection

Fines generated at the discharge of pulp from the refiner were collected by sequentially placing the fabricated sieves of 250-, 300-, and 400- mesh screens at the discharge of the 200-mesh sieve (76 μm x 76 μm). These were stainless steel square opening mesh sieves with 63 μm x 63 μm, 53 μm x 53 μm, and 37 μm x 37 μm square

apertures corresponding to 250, 300, and 400-mesh, respectively. The collected fines, therefore, are associated with pulp mass separated by their width and length, based on the Sherwood Fiber Quality Analysis principle – see Table 2. These were retained on specific mesh sieves due to their inability to escape the 76 μm aperture of the 200-mesh screens trapping the accepts. The fines collected on the respective sieves are therefore denoted P200/R250, P250/R300, and P300/R400 with P denoting 'pass' and R denoting 'retain'. Both the accepts and collected fines constitute 95% yield of the attempted APMP of EFB with loss having association with 1.5% extractives from dewaxing stage, about 1% minerals and 2.5% fines and other organics escaping 400-mesh sieve. Based on the 12-20% range of fines by the 3 mesh fractions, the R200-to-fines fines proportion is approximately 60:40.

Making of Handsheet

Handsheets were prepared in accordance to the TAPPI procedure (TAPPI 1997). Where fines were incorporated, the P200/R250, P250/R300, and P300/R400 fines fractions were added before mixing the slurry using a Toyoseiki disintegrator. Handsheets prepared with the unscreened pulp were labeled A, while those prepared with R200 were labeled B. Samples containing blends of R200 with 12% of fines: R200+P200/R250, R200+P250/R300, and R200+P300/R400, were labeled B250, B300, and B400, respectively. The fines proportion was selected based on the 10 to 30% range of fillers used in commercial papers. The selected lower level was also to ensure utilization of fines generated per batch of pulping and to rule out the need to run pulping specifically to generate fines.

Five different sets of handsheets with 10 to 15 sheets per set were prepared and tested for their mechanical properties in accordance to TAPPI Test Method T 511 for folding endurance, T 414 for tearing resistance, T 403 for burst index, and T 494 for tensile index. Optical properties were examined by TAPPI test method T452. All density values are measured as sheet weight per volume of handsheet, where volume is the multiplication product of sheet area and sheet thickness.

Microscopy and Fiber Analysis

Fines were examined qualitatively using a light microscope with four lenses fixed at the rotating nosepiece. All slides were labeled accordingly and analysis of fibers was performed without staining. Transmission light microscope interfaced with an image analyzer was then run to analyze the fibers. SEM or scanning electron microscopy was run on the 30 nm gold-coated handsheet samples using a Carl Zeiss Leo Supra 50VP to check for evidence of fines entrapped in the pulp network.

Fibre dimensional characteristics were acquired from Sherwood FAS-3000 Fibre Analysis System (USA), and this analysis was performed on pulp suspensions (pulp and fines) as recommended by the instrument manufacturer. Quantitative proportion of the fines was also obtained from this analysis.

RESULTS AND DISCUSSION

Fibres and fines differ in structural properties (Gorres *et al.* 1996) and morphology. While fibres making up the accepts are pulp mass retained on the 200-mesh screen, fines are the fibrous particles passing a 200-mesh sieve. The ability of long fines structures to escape the aperture also reflects their degree of flexibility (Subramanian *et al.* 2008).

Characterization of Fines in Screened Pulp

The refined EFB mass collected as 200-mesh pulp fraction, or "accepts" denoted as R200, show the presence of fiber and fiber bundles. Fiber bundles, which occurred as a result of EFB segmentation rather than lubricated shearing of EFB vascular bundle, were found in lengths of 400 µm (Fig. 1a) and 1000 µm (Fig 1b) and of about 200 µm width, by direct two-dimensional micrographic measurement. Also predominant in the R200 mass were the long tube-like and tapered vessels in the form of bordered pits (Figs. 1c and 1e) and besides the segments of 260 µm (Fig 1c) and 420 µm (Fig 1d), vessels elements up to approximately 600 µm was also encountered as a result of segmentation

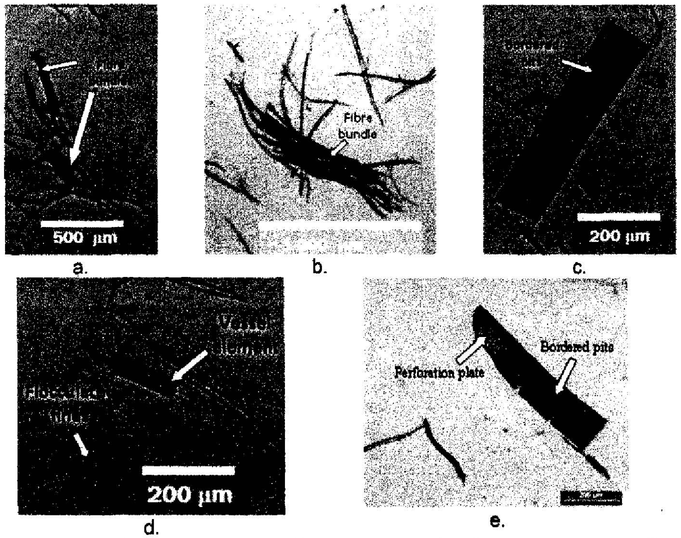


Fig. 1. Fines collected together with R200 fraction a) Fibre bundle and fibers, b) Larger fiber bundle (resemble fiber if sheared to single strands of 1 mm fiber) c) vessel elements showing bordered pit d) Flocculated fines e) Bordered pit and perforation plates encountered on vessel element.

of the vessel in the internal structure of EFB vascular bundles. These are the unfibrillated elements in the fibrous mass, marking the failure of vessel and fiber fractions to fibrillate extensively.

Evidence of an intact perforation plate in Fig. 1e is also indicative of poor fibrillation. The smorgasbord of structures suggests the kind of EFB pulp mass passing between the refining plates (Peel 1999), which is believed to be the consequence of refining action (Chevalier-Billosta *et al.* 2007). The abundance of the unfibrillated materials including intact vessel fragments shown in Fig. 1 reflects the rigidity of the lignin-carbohydrate matrix and the inadequacy of biomass softening allowed by the adopted conditions.

Apart from the noted unfibrillated elements, flocculated fines (Fig. 1d) were also present in the R200 mass, plausibly originating from the detachment of long fibrils of EFB vascular bundles, analogous to the fibrillar end of the vessel element in Fig. 1c. This was attributable to the friction between vessel elements and the refining plates, resulting in shear instead of segmentation, due to the presence of residual alkaline peroxide. Although resembling fibrils, the coiling conformation of about 60 µm with surrounding fine web attributable to external fibrillation had apparently denied successful passage through the 107 µm diagonal of the aperture of the 200-mesh sieve

Unlike the R200 pulp fraction, which is insignificantly different from the P200/R250 fractions, both Fig. 2a and Fig. 2b show fines characteristic of xylem vessel elements of the P250/R300 fines fraction, demonstrating extensive fibrillation. Evidence of a broom-end structure in Fig. 2a is one demonstration of fibrillation of the fibril (vessel strand) arising from 'splitting' along vessel pits. This resulted in pulp mass in the form of a fiber or single strand, insufficiently thin (75 µm x 75 µm unfibrillated vessel and 500 µm x 10 µm fibril) to escape or long enough to tangle and thus, retained on the 300-mesh screen of 53 µm x 53 µm aperture with 75 µm diagonal. Noteworthy, however, is the fact that fiber bundles encountered in this mesh fraction contained a lower count of fiber in a bundle, suggesting lower-width mass with more flexibility to escape the 250-mesh sieve.

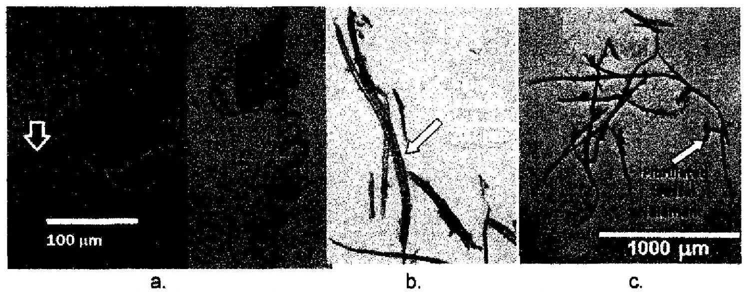


Fig. 2: Fines of P250/R300 consisting of a) semi-split xylem vessel with broom-end (arrow) and a more pronounced splitting of vessel resembling fibre of spiral conformation (x10) on the right, b) two semi-detached stands of fiber in a bundle and c) segmented spiral fibril hooked to long fibers (x4).

Intact vessel elements were also scarce, except for those dangling with long spiral fibrils (Fig. 2a) possessing length typical of EFB chemical pulp fiber. Figure 2c shows the relative sizes of fibers and fines in the form of segmented vessel fibril. Spiral conformation increases the possibility of hooking to fibers and retention in the R300/P250 fines fraction. Under the influence of their length, these are unlikely to fill up micro-voids but likely to promote good paper formation by creating sites for gluing onto multiple fibers.

Fibrous mass of reduced dimensions were commonly encountered in the P300/R400 fines fractions (Fig. 3). These are segments of vessels, fibers, fibre bundles, and fibrils. Segmentation of fibrils of the vessel elements left behind vessel flakes of 74 µm x 76 µm dimensions (insert in Fig. 3) that may have adequate curving capacity to escape 300-mesh sieve of 75 µm diagonal aperture. On handsheets, flakes were observed to adhere onto fibre surfaces, visible as patches of vessel element (Figs. 4c and 4d), and likely to impose high picking tendency in the offset lithographic printing (Colley 1973). As in the case of flakes, likewise the liberated fibrils that have undergone severe rupture apparent from the web-like appearance, as indicated by circles in Fig. 3c, are unhelpful in promoting sheet strength. These are elements responsible to the acclaimed 'fiber coalescence' commonly encountered on the surface of EFB pulp handsheets of tensile index above 15 Nm/g (Ghazali *et al.* 2011; Dermawan and Ghazali 2011). By masking of individual fiber strands and promoting sheet cohesion, the pulp network appears smoother. Finer materials with broom-end features of submicron fibrils that are signs of severe shearing forces or segmentation upon shearing of individual fiber and vessels also promote inter-fiber bonding due to their chances of clinging onto adjacent fibers.

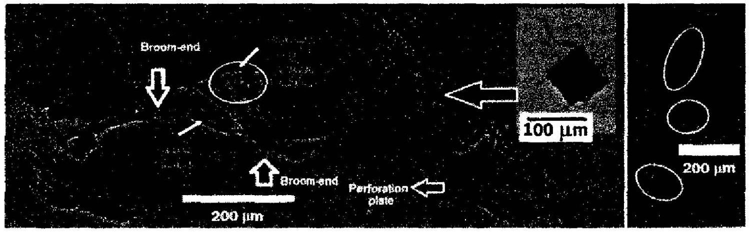


Fig. 3: Fines collected as 400-mesh fractions showing mixture of completely 'split' xylem vessel, fiber bundle and fibre fragments (Insert)(x4).

Table 1 sums up the approximate size of the vessel elements in the respective mesh fractions. Although the relative sizes of the unfibrillated and fibrillated elements correlate with the predicted shearing severity undergone by the biomass, the relative sizes of micro-gaps are more influential in determining the more desirable fines dimension. Despite being most slender, for instance, P250/R300 fractions offer less of filling effect in comparison to the P300/R400 fraction but served more as a binder due to the presence of long fibrils (Fig. 2a) and more binding sites. These are even enhanced by the existence of submicron fibrillated fibrils evident as a broom-end structure in Fig. 2a.

Table 1. Approximate Dimensions of Vessel Elements in Fines Fractions

Fines Fraction	Predominant Vessel Dimension					
	Unfibrillated		Fibrillated			
	Length, µm (±10 µm)	Width, µm (±10 µm)	Length, µm (±50 µm)	Width, µm (±5 µm)	Approximate Slenderness Min	Approximate Slenderness Max
200-mesh	100-600	20-150	200-1000	5-20 µm	10	200
300-mesh	60-75	50-75	400-1500	7-10 µm	40	214
400-mesh	65-80 50	15-73 50	100-300	5-7 µm	14	60

Diagonal of stainless steel square mesh aperture:
200-mesh (76 µm x 76 µm): 107 µm
250-mesh (63 µm x 63 µm): 89 µm
300-mesh (53 µm x 53 µm): 75 µm
400-mesh (37 µm x 37 µm): 52 µm

NB: Nature of Fibrils
200-mesh: very uncommon
250--mesh: partially detached to vessel
300-mesh: partially attached to vessel
400-mesh: detached from vessel & segmented.

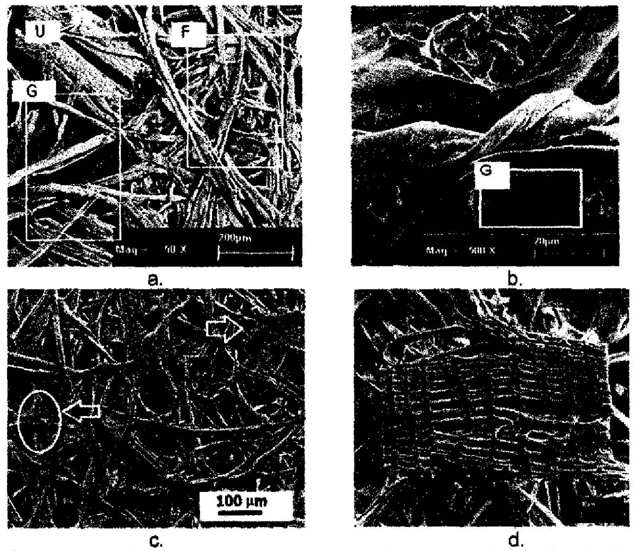
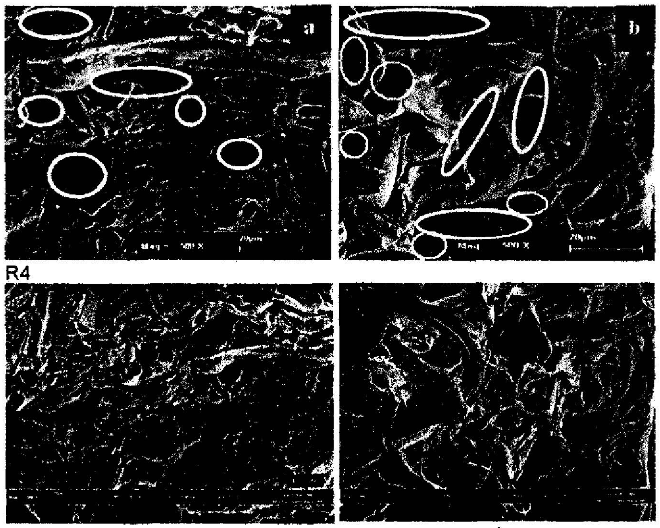


Fig. 4. Micro--void (G) and filled gaps (F) in the studied pulp network a) G, F and unfibrillated bundles (U), b) close up of smaller gaps, which is less likely to accommodate fines c) vessel on surface of pulp network d) close-up of vessel on pulp network marked by circle and arrows in c.

The found fines elements, however, are much better in reinforcement of pulp network strength in comparison to ray cells, which according to Sundberg and co-workers (2003) are of no aid to pulp network strength improvement. The vessel-rich mass from APP of EFB is likely to impose a different extent of pulp network improvement, depending on the nature of the gap created by the incompletely fibrillated mass. This is revealed in Fig. 4, which demonstrates gaps or micro-voids (G) in handsheets arising from oversized elements in the pulp mass, U, which is in close association to the partially ruptured vessel elements in the R200 pulp fraction in Fig. 1e or the unfibrillated portion of vessel in Fig 2a. From the relative sizes of gaps (Fig. 4) and fines (Table 1), it is plausible that the smaller fines stand higher probability of acting as voids filler. Present in invariable shapes, gap areas ranging from 10 μm^2 to more than 200 μm^2 are more likely to be densely filled with the P300/R400 fines fraction than the P250/R300 fines fraction. The relative compactness of the said fines is reflected in Fig. 5a and Fig 5b, with smoother and denser appearance depicted on the P300/R400 fines in comparison to the higher count and the larger size of the micro-voids within the P250/R300 fines cluster. In addition, the higher coarseness or bulk implied by the higher extension of fines-air interface in the P250/R300 fines in Fig. 5a is attributed to the loose volume caused by the long spiral structure of the vessel element previously presented as Fig. 2a.



a. b.

Fig. 5. Scanning electron micrographs emphasizing count and size of micro-voids marked by circles and ovals: a) R400/P300, b) R300/P250 fines, at x500 magnification, with close-up look at the top and larger viewing area below

Table 2 also presents changes in optical and mechanical properties of handsheets upon addition of fines. The increase in brightness as a result of adding fines is a signal of good reaction between peroxide and fines. This suggests the predominance of surface lignin, to which peroxide is prone (Asikainen *et al.* 2011). The findings therefore map surface lignin as residing in the fibrillated vessel elements and fibrils (Figs. 2a and 3). With more gaps accommodated by fines, reduction in sheet porosity and enhancement in opacity indicated in Table 3 suggest improvement in inter-fiber bonding.

Without fines, screened pulp (Sample B), however, offered the lowest tensile and tear indices due to poor inter-fiber bonding. Low extent of fibrillation, which resulted in the predominance of unfibrillated structures and fibre bundles (Fig. 1) was the key factor and this reflects the rigidity of the lignin-carbohydrate matrix and the inadequacy of biomass softening allowed by the adopted conditions. The principal reason for occurrence of these fiber bundles was inadequate reaction between alkaline peroxide and EFB that would otherwise soften the biomass and facilitate fibrillation process. One way to improve this is by applying alkaline peroxide during the refining process, similar to the concept of PRC-APMP™ (Xu, 1999b; Xu *et al.*, 2000b), the results of which will be discussed elsewhere.

As far as mechanical strengths are concerned, tear index improved by 15%, and this is only 0.1 point inferior to the whole (unscreened) pulp network of Sample A, suggesting that the individual fibres were more difficult to pull from the network of native fibrous mass blended with size-specific fines fractions. The better strengths as a result of enhancement in inter-fiber bonding and reduction of sheet porosity as also implied in the higher density of handsheets prepared with fines addition. Similar behaviour was also portrayed by the highly fibrillated fines of bleached softwood kraft pulp reported by Subramanian and team (2008).

Incorporation of the P200/R250 fines fraction in Sample B250 led to 61% (relative to Sample B) enhancement of tensile index, quantitatively suggesting a positive effect of fines, although this effect is difficult to delineate from qualitative microscopic observations. This was also demonstrated by the initiation of folding resistance.

Blending the R200 pulp with P250/R300 and P300/R400 fines fractions improved tensile index by 75% and 100%, respectively. This demonstrates the strength enhancing effects of the fines collected from the APMP of EFB, which were evidently vessel elements. The sheared vessel elements splitting along the perforation lines resembled thin, long fibres [*cf.* EFB fiber: 1000 µm length, 20 µm diameter (Law *et al.* 2007)] possessing better flexibility and collapsibility, which are likely to enhance inter-fiber bonding filling of micro-voids and acting as connecting medium. This renders better pulp consolidation, enhanced sheet cohesion and thus, an increase in tensile strength. Similar observation was also reported by Sirvio and Nurminen (2004) and Rousu and Niinimaki (2005) for inter-fiber bond enhancement by wood fibrillar fines and parenchymatous and epidermal cells monocot non-wood (common reed and wheat straw) pulp fines, respectively.

Besides the well fibrillated structures (Fig. 2), other fragmented mass constituting the finer pulp mass indicated in Fig. 3 were mainly responsible for filling the gaps between the R200 pulp of EFB. This pulp mass, which is predominantly fines and short fibres, are shorter (Table 2, Pulp Fractions), resembling the more pronounced segmentation and shearing undergone by the 300-mesh fines fractions. Owing to their higher surface areas, other than acting as filler, these elements also provided contact for enhanced fibre-to-fibril and fibril-to-fibril bondability (Fig. 5) and overall pulp network strength. Considering that a CSF value of 580 to 530 mL is an acceptable range of pulp drainability, the findings point to the practicality and the high potential of fines as pulp strength reinforcement filler with acceptable practicality. The reverse effect may be imposed by higher mesh fines fractions due to challenges with pulp drainability during paper product fabrication and the natural tendency of these finer materials to adsorb unwanted materials (Ahmad *et al.* 2011) and introducing foreign materials such as leached extractives (Luukko and Paulapuro 1999) to the resultant product.

Table 2: Selected Properties of Pulp and Handsheets

	Samples				
	A	**B**	**B250**	**B300**	**B400**
CSF (ml)	710	580	564	550	530
% Pulp Fractions					
Fines	N/A	16.4	N/A	18.5	22.9
Short*	N/A	21.8	N/A	26.2	29.2
Medium**	N/A	50.8	N/A	46.8	42.9
Long***	N/A	7.7	N/A	5.6	3.7
Density (g/cm^3)	0.222	0.230	0.244	0.253	0.254
Tensile Index (Nm/g)	4.3	3.6	5.8	6.3	7.2
Tearing Index (mNm^2/g)	3.9	3.3	3.8	3.8	3.8
Folding Endurance	0.00	0.00	1.4	1.7	1.9
Brightness (%ISO)	44.9	44.4	46.4	46.5	46.9
Print Opacity	88.21	89.78	93.55	93.64	94.72
Tappi Opacity	81.13	83.00	89.27	90.71	90.57

Key:
A = whole pulp
B = screened pulp
B250 = B + 12% P200/R250 fines fraction
B300 = B + 12% P250/R300 fines fraction
B400 = B + 12% P300/R400 fines fraction

Fines = width 3-60 μm;length < 0.112 mm
*Short = width 3-60 μm;length 0.112-0.448 mm
**Medium = width 3-60 μm;length 0.560-1.456 mm
**Long = width 3-60 μm;length 1.568-7.168 mm
N/A = Not available.
*, **, *** dimensions defined by FQA data.

CONCLUSIONS

1. EFB handsheets blended with the smallest of the examined fines fractions (P300/R400) showed enhanced pulp network strength associated with tensile index and folding endurance.
2. Reinforcement fibers in the P300/R400 fines fractions were the segmented vessel fibrils characterized by their minimal length and diameter that were also the key factors enabling them to accommodate the micro-voids commonly found in the network of pulp produced by the adopted method.
3. Besides acting as filler, pulp network strength was also improved by the long fibrillated vessels in the P250/R300 fines fraction due to their high surface areas

serving as fibers bonding sites. External fibrillation of these produces submicron fibrils was also able to improve fibre network by their web structure.

4. This study identified and characterized desirable fines whose collection and utilization enable maximization of process yield and minimisation of waste from APP of EFB pulping line.

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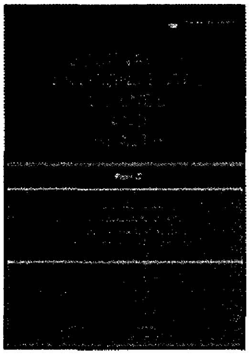
APPENDIX $ _ PAPER $



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Removal of Pesticides from Water and Wastewater by Different Adsorbents: A Review

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Removal of Pesticides from Water and Wastewater by Different Adsorbents: A Review

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In this review article, the use of various low-cost adsorbents for the removal of pesticides from water and wastewater has been reviewed. Pesticides may appear as pollutants in water sources, having undesirable impacts to human health because of their toxicity, carcinogenicity, and mutagenicity or causing aesthetic problems such as taste and odors. These pesticides pollute the water stream and it can be removed very effectively using different low-cost adsorbents. It is evident from a literature survey of about 191 recently published papers that low-cost adsorbents have demonstrated outstanding removal capabilities for pesticides.

Keywords: adsorption; pesticide; low-cost adsorbents; agricultural wastes

1. INTRODUCTION

During the latter half of the nineteenth century, along with the rapid expansion of the chemical manufacturing industry, environmental pollution events occurred frequently. Several dramatic accidents such as oil spills happened in the 1970s and now in 2010 made the perception of environmental deterioration flourish. By the 1980s, diffuse pollution, particularly long-range transport of atmospheric pollutants, exemplified by acid deposition, was identified as a serious environmental and ecological issue [1]. The release of methyl isocyanides (MIC) by Union Carbide factory accident in Bhopal was one of the worst examples of disaster and widespread pollution. During the past 20 years, concern has arisen due to the presence of pesticides in the environment and the threat they pose to wildlife and mankind.

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Chemical pesticides have contributed greatly to the increased yields in agriculture by controlling pests and diseases and also toward checking the insect-borne diseases (malaria, dengue, encephalitis, filariasis, etc.) in the human health sector [2]. The need to increase world food production for the rapidly growing population is well recognized [3]. However, the sporadic use has been leading to significant consequences not only in public health but also in food quality, resulting in an impact load on the environment and hence the development of pest resistance. Through overuse and misuse there is considerable waste, adding to the cost and contributing to the adverse environmental and health consequences. Inappropriate application of pesticides affects the whole ecosystem by entering the residues in the food chain and polluting the soil, air, ground, and surface water [4, 5].

The term "pesticide" is a contraction used to define a variety of agents

of agricultural waste.

Finally we wish to comment on the zero waste strategy of the adsorption process in treatment of water and wastewater. There is a bigger scope of research of utilization of used adsorbents for further treatment processes. For example pesticide adsorbents can further be explored for their application in second-stage adsorption, which is a completely unexplored area of research. Another possibility of exploration is the recovery cum reuse of adsorbed substances. All future research might be accompanied by the adsorption/desorption and/or adsorption/re-adsorption process so that there is little, if any, net sludge generation. Such a strategy will fulfill the goal of zero waste.

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EFFECTS OF MULTIPLE CHEMICAL IMPREGNATION ON APP OF EFB

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A simple pulping method, defined as alkaline peroxide pulping (APP), which integrates both pulping and brightening actions into a single process, was attempted on abundant industrial waste – the oil palm empty fruit bunch (EFB). Originating from alkaline peroxide mechanical pulping (APMP), the major processes making up an APP system involve impregnation of alkaline peroxide (AP) into the biomass prior to refining, to finally yield APP pulp. By applying alkaline peroxide at a 2:2.5% (wt/wt) alkali-to-peroxide ratio, one-stage impregnation gave an EFB pulp brightness of 55% ISO. The subsequent impregnation stages offered 68 and 70% ISO for two- and three-stage impregnation, respectively. In fact, the said optical property and other mechanical properties of the sheets prepared via two-stage and three-stage 2:2.5% (wt/wt) alkali-to-peroxide impregnations also showed better results, as compared to those of the one-stage treatment with 4:4.5% (wt/wt) alkaline peroxide. The results of the two-stage impregnation of AP, prepared at a high concentration of 4:5% (wt/wt) alkali-to-peroxide ratio, also showed improvement in the sheets' mechanical properties, as compared to those of the one-stage process. This demonstrates the advantage of maximizing the AP chemical power by mechanical forces that could enhance its accessibility to EFB structures, rather than increasing the AP dose for attaining the same effect. Maximisation of AP is particularly important for reaching the expected sheet properties, while ensuring the eco-friendliness of an APP system.

Keywords: alkaline peroxide, pulping, APP, APMP, EFB, impregnation, paper properties

INTRODUCTION

The oil palm empty fruit bunch (EFB), an abundant biomass waste, available throughout the year, was subjected to an attempted conversion into a value-added material. Known by its scientific name[1] of *Elaise guineensis*, this initially ornamental plant of West African first came to Indonesia in 1848 and to Malaysia in 1911, as cash crop. Today, Malaysia and Indonesia are world leading producers of palm oil and cellulosic biomass, known as EFB.

In the effort of utilizing the biomass for preventing its accumulation, EFB was tested for the production of panel products,[2] ash glaze,[3] animal feed,[4] and briquette as biofuel feed.[4] Out of all these, the pulp production offers the most significant cash return, due to both high yield and attractive existing market price per ton of material.

To further enhance the attractiveness of the cash return, a low cost and high yield process would help do the trick. An example of such a process is predictable for Alkaline Peroxide Mechanical Pulping (APMP), which was first introduced[5] by Andritz Sprout-Bauer in 1989, as an improvement of the Chemi-Thermo-Mechanical Pulping (CTMP) process. In an early stage, the process was used in wood pulping. Maple,[6,7] birch[6,7] aspen[5] and poplar[8] biomass were recording successful APMP pulp production. Later, non-wood species, such as jute,[9] kenaf,[10] straw[10] and baggase,[11] further extended the list of successes, evidencing the flexibility of the process in pulp property development.

Enticed by the successful attempts recorded in literature, the concept of APMP was applied on EFB with processes that mimicked the working principle of APMP. For making use of rather different gadgetry, the system designed for EFB pulping is abbreviated as APP, to denote alkaline peroxide pulping. This paper reports the possibly acquired high-end properties of the APP pulp from EFB, coupled with an environmental control of the process.

EXPERIMENTAL

Raw material preparation

The vascular bundles of EFB – the raw material selected for the study – were obtained as bales. These were loosened, washed thoroughly and air-dried before grinding to 500-micron particles. Dewaxing was done by soaking the biomass particles in distilled water at 70 °C for 30 min, for removing 50% of the extractive components. At the end of the dewaxing process, the biomass particles were demoisturized by pressing at 15 psi.

Alkaline peroxide impregnation

The alkaline peroxide (AP) was prepared by premixing hydrogen peroxide and sodium hydroxide of Merck Schuchart, Germany. By weight percentages, the selected alkali-to-peroxide ratios were of 2:2.5, 4:5 and 10:11%. The reaction was allowed to proceed for 40 min at 70 °C, after which the biomass was again pressed at 15 psi and the liquor was collected for analysis. To achieve multiple impregnations, the process was repeated by applying fresh chemicals on the biomass.

Refining and making of handsheets

Refining was conducted with a Sprout Bauer Refiner, to allow fibrillation. The fibres obtained were made[12] into handsheets, according to TAPPI Test Methods 1997.

Mechanical and optical testing

The mechanical testings conducted in the study involved folding endurance (TAPPI 511), burst index (TAPPI 403), tensile index (TAPPI 494), tear resistance index (TAPPI 414) and zero span strength (TAPPI 231), while optical testings included brightness and opacity of handsheets (TAPPI 452). These were all compiled in TAPPI Test Methods 1997.

Spent liquor analyses

The COD, TDS and turbidity of the pulping spent liquor batches were analysed by the methods of the American Environmental Protection Agency (EPA). Residual peroxide was determined on a Shimadzu UV-Visible 1601PC Spectrophotometer, based on the method of Chai,[13] for accuracy, simplicity and rapidity.

RESULTS AND DISCUSSION

Spent liquor analyses

The spent liquors resulted from alkaline peroxide pulping (APP) of EFB contained leaching materials, such as residual extractives, inorganics, residual alkaline peroxide, as well as other organic compounds, like lignin and modified lignin, produced by the reaction of chromophoric groups from the lignin structure with alkaline peroxide.[14-15]

The role of alkaline peroxide in fading the colour of lignin is more dominant than removing of lignin from the EFB structure, which resulted in spent liquor with lower COD, turbidity and TDS – compared to other pulping processes.

As shown in Figure 1, the spent liquor from the first stage showed the highest COD and TDS, which were attributable to leaching of materials, such as lignin, extractives and other organics, and to inorganics, such as silica, which were more loosely bound to EFB after a second impregnation pressure of 15 psi. Meanwhile, the highest turbidity in the second stage of impregnation might have contributed by the release of silica, being possibly dislodged by mechanical actions,[16,17] as well as other minerals liberated from the EFB strands.

The residual peroxide plotted in Figure 1 (d) reflects both the way in which AP impregnation occurred, and also the effect of the multiple impregnation stages. Residual peroxide was the highest in the liquor collected from the first stage impregnation, and the lowest after the third impregnation stage.

Stiffness of the EFB strands in the first stage AP impregnation might explain the poor consumption of peroxide in the first impregnation. The presence of residual extractives and silica in the craters might have also hindered the penetration of the AP chemical into the fibre wall, thus hindering the brightening effects.

Subsequent impregnations, however, allowed more access of AP to the fibre strands, favouring more handy reactions between AP and the active sites of EFB and, consequently, lower values of residual peroxide. Softening of the EFB strands could have liberated more silica bodies from their crater – as a synergistic effect of mechanical pressing, which had generated numerous macro- and micro-ruptures. Softening, on the other hand, arose from the liberation of lignin, which was initially the adhesive contributing to the contracting forces of the fibre.[18-19] Lignin removal itself was affected by the space between lignin molecules, relative to the pore size of the fibre wall.[18] Thus, by removing lignin, the new available space allowed more occupation of the active alkaline peroxide species which, in turn, triggered increased lignin removal from EFB. Besides lignin removal, the alkali in AP could also have access to the fibre wall, thus deliberately softening the biomass strands.

The loss of unwanted materials was in line with the declining values of yield with the number of AP impregnation stages (Fig. 1).

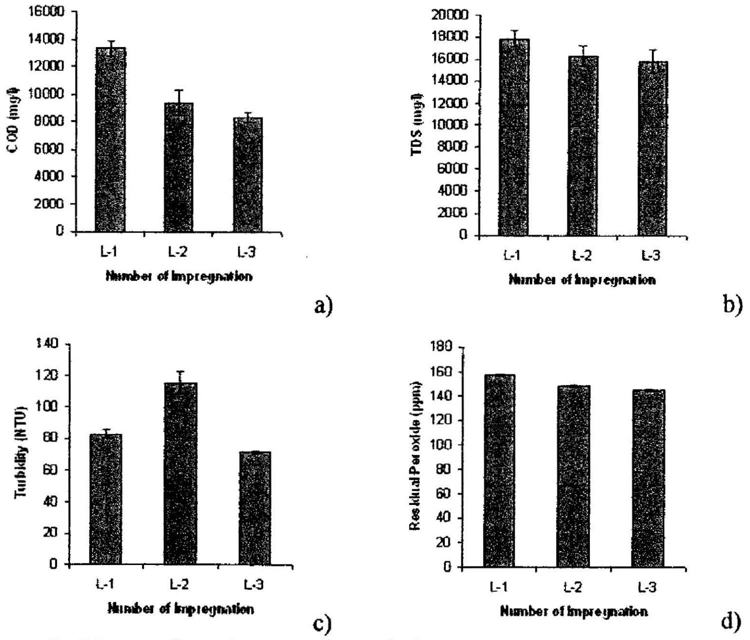

Figure 1: Liquors from impregnation of EFB with 2:2.5% (wt/wt) alkaline peroxide analysed for (a) COD, (b) TDS, (c) turbidity and (d) residual peroxide; L-1 – spent liquor from one-stage impregnation; L-2 – spent liquor from two-stage impregnation; L-3 – spent liquor from three-stage impregnation

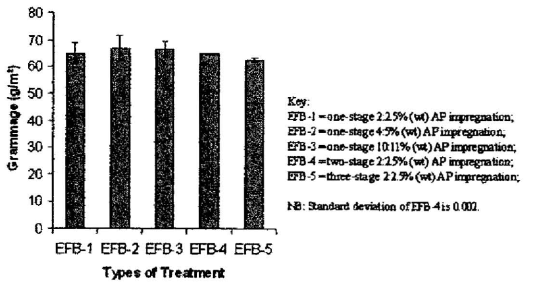

Figure 2: Grammage of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

Mechanical properties

For a handsheet grammage of 63±2 g/m^2 (Fig. 2), folding endurance, which is the reflection of fibre and handsheet elasticity,[20] was seen as appreciably affected by the chemical level and impregnation stage. Consistent with the high stiffness, difficult to fibrillate and thus, with low access of alkaline peroxide (AP) into EFB strands, the handsheet prepared from EFB impregnated with a 2:2.5% (wt) alkali-to-peroxide ratio had, as expected, lacked of folding endurance (cf. EFB-2, which was impregnated with 4:5% (wt) AP).

When the AP level was increased to a 4:5% (wt) alkali-to-peroxide ratio, the fibre became softer and more fibrillation was expected to be generated upon refining. On the contrary, above a 10:11% (wt) alkali-to-peroxide ratio, the folding endurance of the handsheet decreased, which could be prompted by a higher generation of fines instead of fibrils, due to severe causticity, which triggered heating of AP in the EFB particles, thus accelerating cutting of fibres. The main cause of heating of the refining plate was its friction with residual chemicals and biomass during refining.

At a 2:2.5% (wt) alkali-to-peroxide ratio, the handsheet prepared from two-stage AP impregnation showed the highest folding endurance, indicating a better sheet elasticity. The sheet produced from two-stage AP impregnation evidently offered high zero span strength, as well as high burst and tensile indices. Three-stage AP impregnation, on the other hand, could develop a better sheet resistance to tearing (Fig. 3d). Sufficient fibre length, better network, or the synergistic effect of fibre bonding and fibre length mostly influenced the high tear strength. From this point of view, three-stage impregnation offered relatively better tearing resistance in comparison to two- and one-stage impregnation (despite the increased AP level).

Optical properties

Figure 4 illustrates the optical properties of the handsheet, exhibiting a strong relationship with the physical properties.

Handsheets prepared from one-stage 2:2.5% (wt) alkali-to-peroxide seemed high in opacity (95% for TAPPI Opacity and 93% for Print Opacity). Additional impregnation stages, as well as the increase in AP concentration apparently hampered Print and TAPPI Opacity by 14 and 7 points, respectively, with reference to EFB-1 and EFB-5. This may only be applicable to the 2:2.5% (wt) AP, and an extended study is needed to ascertain if the effects are also applicable to other higher AP strengths.

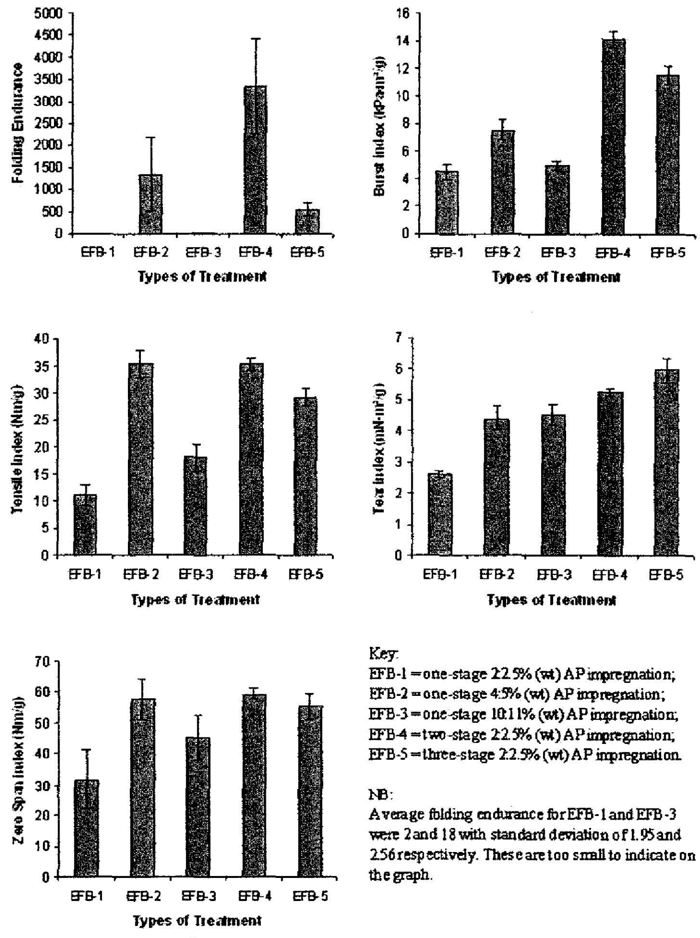

Figure 3: Mechanical properties of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

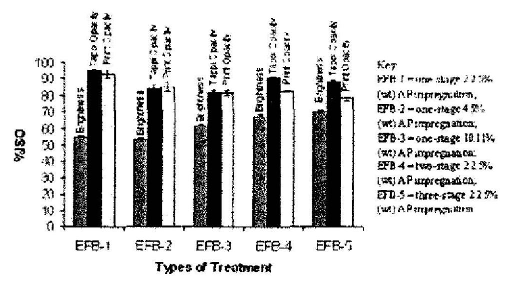

Figure 4: Optical properties of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

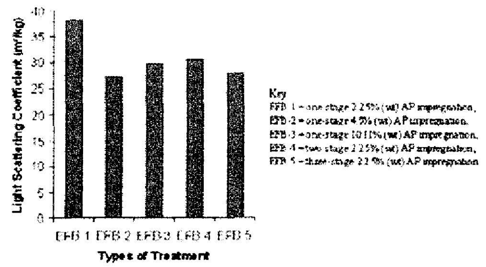

Figure 5: Light scattering coefficient of handsheets prepared at varying AP levels and by varying stages of impregnation (for 2:2.5% (wt) AP)

The highest brightness, of 70% ISO (Fig. 4), was possibly acquired by a three-stage 2:2.5% (wt) alkali-to-peroxide impregnation process, while the lowest brightness, of 53% ISO, was offered by one-stage 4:5% (wt) alkali-to-peroxide impregnation. The data suggest that an increase in the chemical level may not be a measure for enhancing brightness. A more efficient means of enhancing brightness was to maximize the lower level AP chemical power, by triggering access of the chemical to the more hidden interior of the biomass. Alkaline peroxide of 2:2.5% (wt) alkali-to-peroxide was apparently sufficient to trigger a pronounced brightening effect, by applying a pressure of 15 psi onto the softened EFB in the second and third impregnation stages. This was apparently an effective measure, evident for brightness enhancement from 55% ISO in one-stage AP impregnation to 68% ISO in two-stage impregnation and to 70% ISO in subsequent pressurised AP impregnation.

The results for the light scattering coefficient also consistently favoured the 2:2.5% (wt/wt) alkali-to-peroxide ratio, provided that AP impregnation was done under the established pressure. The factor behind this is also the effectiveness of chemical penetration into the biomass, which would in turn soften the inner structure, facilitate fibrillation and inter-fibre bonding. The application of pressure as a mechanical way for promoting accessibility of AP into EFB also helped maximization of AP power. Residual alkalinity from AP, for instance, could induce alkaline darkening, typical for the isolated action of the hydroxyl ion on a chromophoric group in the biomass.[21] Similarly, residual alkalinity could also trigger darkening of biomass through re-deposition of leaching materials onto the EFB surface,[22] which could in turn result in biomass stiffness and poor fibrillation during refining. As to the darkening phenomenon, raising the ratio of alkali might have therefore increased the chances of alkaline darkening, as evident for the lower LSC obtained from AP impregnation at an alkali-to-peroxide ratio higher than 2:2.5%.

The Kappa number corresponding to these handsheets was of 101.4 for one-stage impregnation of 10:11 alkali-to-peroxide, while subsequent impregnations of the same AP level could reduce the Kappa number to 82.3, and further down to 75.3, for three-stage AP impregnation. This may in a way support the possibility of achieving an 80% ISO brightness, if subsequent pressurized impregnation of the same AP level was applied on the biomass. The contradictory trend of brightness could be explained by the light scattering coefficient (LSC) values. At the same level of chemicals, two-stage impregnation offered 30.7 units for LSC, while subsequent impregnation resulted in 26.7 LSC units. The reducing value of LSC implies reducing smoothness of the handsheet, arising from the gaps between fibres, which could be due to the non-uniformity of the fibre sizes.

As to delignification, it could be also observed that, with the release of leaching materials, more available spaces could be created between the pore size and the lignin molecules. This opened up more chances for hemicelluloses (hydrophilic hemicelluloses, especially,[5] and other substances in the fibre) to react with the chemicals. An evidence of recalcitrant residual lignin, therefore, suggests the dissimilar sizes between the lignin molecules and the available pores, which could be the factor limiting the AP access into the residual chromophoric groups. In relation to release of organics, however, the COD and TDS contents in the spent liquor after the third impregnation stage could be thus mainly attributable to the hemicelluloses squeezed out of the biomass. This further demonstrates the sufficiency of the two-stage 2:2.5% (wt) alkali-to-peroxide impregnation (rather than a higher chemical dose) for brightness improvement, while sustaining the mechanical strength of the handsheet.

CONCLUSIONS

COD, turbidity, TDS and residual peroxide offered a simple way of checking the sufficiency of the alkaline peroxide level and impregnation stages in an alkaline peroxide pulping system, involving the extent of removal of unwanted substances, such as lignin, inorganics and extractives. The level of alkaline peroxide used and the number of impregnation stages could be adjusted to achieve the desired properties of the resulting pulp. Apparently, an additional impregnation stage for 2:2.5% (wt) alkali-to-peroxide could be more effective than an increment in the alkaline peroxide level, suggesting that the chemicals have to be maximized by enhancing their penetration into the EFB biomass. The mechanical forces involved during impregnation (15 psi pressure) allowed access of chemicals to a larger biomass area, and also triggered a better release of unwanted materials. Multiple-stage impregnation of 2:2.5% (wt) alkali-to-peroxide is therefore recommended for the production of high brightness pulp with overall good mechanical properties.

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Characterization and adsorption kinetic study of surfactant treated oil palm (*Elaeis guineensis*) empty fruit bunches

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ABSTRACT

Oil palm (*Elaeis guineensis*) empty fruit bunches (OPEFB) was treated with cetyltrimethylammonium bromide (CTAB) to make its surface suitable for methyl orange (MO) dye adsorption. CTAB-treated OPEFB samples were characterized for their surface functional groups using FTIR, pHzpc, proton-binding capacity, and Boehm titration techniques. The surface morphology and elemental composition of the sample were also studied, employing field emission scanning electron microscopy and energy dispersive X-ray spectroscopy (EDS). It was found that in totality, acidic surface functional group increased after CTAB treatment. The adsorption process was well explained with pseudo-second-order kinetic model. The obtained equilibrium sorption data were then analyzed using the Langmuir, Freundlich, Dubinin–Radushkevich, and Tempkin isotherms. The results showed that sorption was surfactant dose dependent and adsorption increased with an increase in the percentage of surfactant applied on the OPEFB. The maximum adsorption of MO was found at 1% surfactant treatment dose. It was also determined that MO adsorption onto the OPEFB treated with 1% CTAB solution (1% CTAB-OPEFB) followed the monolayer (Langmuir) adsorption. The maximum adsorption capacity of 1% CTAB-OPEFB for the removal of MO was found to be 18.08 mg/g at 298 K (at pH 6.3). Thermodynamic study revealed that the adsorption process was spontaneous and exothermic in nature. There was no energy barrier to initiate the adsorption of MO dye on the CTAB-treated OPFB.

Keywords: Adsorption; Isotherm; Methyl orange; Oil palm empty bunches; Surfactant; Cetyltrimethylammonium bromide

1. Introduction

It is a known fact that the presence of dyes in a water system is hazardous to the environment and human beings. The discharge of dye effluents to the environment is becoming a major concern due to its toxicity. The sources of these dyes are different types of industries such as textiles, dye manufacturing, dyeing, and printing. These dyes can also consume the dissolved oxygen required by aquatic species. Many of them have direct toxicity to microbial populations and even can be toxic and carcinogenic to mammals. The complex aromatic structures of dyes make them more stable and more difficult to remove from the effluents. It is a general perception that water quality is greatly influenced by its color since dye is the first contaminant to be recognized in wastewater. The presence of even small amounts of dyes in water—less than 1 ppm for some dyes—is highly visible and undesirable [1]. Therefore, removal of dye has been a very important but challenging area of wastewater treatment. Several methods including biological and physicochemical technologies have been suggested to remove dyes from wastewater. These processes include coagulation, electro-coagulation, anaerobic include coagulation, electro-coagulation, anaerobic treatment, flotation, filtration, ion exchange, membrane separation, adsorption, and advanced oxidation [2–4].

Currently, there is growing interest in using low-cost, commercially available materials for the adsorption of dyes. The utilization of agricultural wastes for the treatment of polluted water is also an attractive and promising option for the environment. A wide variety of agricultural waste materials are being used as low-cost alternatives to replace expensive adsorbents. Oil palm (*Elaeis guineensis*) agricultural wastes have gained wide attention as effective adsorbents due to its low cost and significant adsorption potential for the removal of various pollutants. Malaysia is one of the largest producers and exporters of palm oil in the world, accounting for 11% of the world's oils and fats production and 27% of export trade of oils and fats. With the growth of palm oil production in fats. With the growth of palm oil production in Malaysia, the amount of residues generated also show a corresponding increase. In Malaysia, oil palm industries are producing substantial quantities of non-oil palm biomass of about 90 million tons of lignocellulosic biomass each year. The empty fruit bunches represent about 9% of this total solid waste production [5,6]. Therefore, attention is given to utilize empty fruit bunches as an adsorbent to clean water.

Many physical and chemical treatments for surface modification of the adsorbent have been invented by the contemporary researchers to enhance the adsorption capacity for dyes removal. Adsorption capacity of agricultural waste is commonly high for cationic dyes, whereas anionic dyes have a relatively low adsorption capacity. This may be due to the fact that the waste's surface is usually negatively charged in natural water bodies, which does not benefit to adsorb anions [7]. Therefore, the surface of the agricultural wastes has to be modified to improve their adsorption capacities for anionic dyes. Therefore, the surfaces of these agricultural wastes are modified by cationic surfactant to improve the adsorption capacity. Recently, some agricultural wastes were modified by surfactant for the removal of anionic dyes, resulting in satisfying adsorption capacities [8–10]. Surface-active substance or surfactants are amphipathic substances with lyophobic and lyophilic groups making them capable of adsorbing at the interfaces between liquids, solids, and gasses. They form self-associated clusters, which normally lead to organized molecular assemblies, monolayers, micelles, vesicles, liposomes, and membranes. Depending upon the nature of hydrophilic group, they can be anionic, cationic, non-ionic, and zwitterionic. The critical micelle concentration (CMC) is the concentration of amphiphilic molecules in solution at which the formation of aggregates such as solution at which the formation of aggregates such as micelles, round rods, and lamellar structures, in the solution [11]. Due to these characteristics, surfactant-modified adsorbents are not only superior in terms of their removal efficiency than that of the conventional adsorbents, but also encourage selective adsorption [12].

The objective of this study was to improve the adsorption capacity of oil palm empty fruit bunches (OPEFB) to adsorb methyl orange (MO). The surface of the OPEFB was modified by impregnating it with the cationic surfactant cetyltrimethylammonium bromide (CTAB). Adsorption capacities of the OPEFB modified with CTAB were also examined under various conditions to evaluate adsorption capacity of MO. Adsorption behavior of the CTAB-modified OPEFB was examined in terms of adsorption isotherms.

2. Materials and methods

2.1. Adsorbent preparation

OPEFB (*E. guineensis*) was supplied by Sabutek Sdn. Bhd., Teluk Intan, Perak, Malaysia. The OPEFB was washed with distilled water to remove dust and soluble substances. The samples were soaked in 0.1 N HCl solution overnight followed by washing to remove all soluble acid impurities. Then, the washed OPEFB was again soaked in 0.1 M NaOH solution overnight followed by washing to remove all soluble base impurities. The samples were dried, ground, and washed thoroughly with distilled water for several times and dried in an oven at a temperature of 60 ± 2°C for 48 h. Then, they were crushed and sieved to produce particles in the range of 150–200 μm size.

For modification of adsorbent, CTAB ($CH_3(CH_2)_{14}CH_2N^+(CH_3)_3Br^-$) (chemical structure shown in Scheme 1) analytical grade from Sigma–Aldrich was used. The OPEFB was modified by cationic surfactant CTAB. Ten grams of OPEFB and 100 mL of different percentage (0.5, 1.0 and 2.0%) CTAB solutions were added to a 500-mL conical flask. The mixture was agitated in a shaker machine for overnight at a speed of 120 rpm. In the next step, suspension was left undisturbed to separate the liquid and the OPEFB from each other. The liquid was discarded, and the modified OPEFB samples were washed with distilled water several times to remove superficially held surfactant and chloride ions. The modified samples were dried in a hot air oven at 343 K for 7 h. The samples of the adsorbents prepared with different percentage of surfactants were coded as 0.5% CTAB-OPEFB for 0.5% surfactant-treated sample, 1% CTAB-OPEFB for 1% surfactant-treated sample, and 2% CTAB-OPEFB for 2% surfactant-treated sample. The selection of modified OPEFB for further study was based on the adsorption performed on different percentage of surfactant.

2.2. Characterization of CTAB-modified OPEFB

Field emission scanning electron microscopy (FESEM) (Carl-Ziess SMT, Oberkochen, Germany) and energy dispersive X-ray spectroscopy (EDS) (Oxford INCA 400 Oxford Instruments Analytical, Bucks, UK) analysis were carried out on untreated OPEFB and CTAB-modified OPEFB samples to study their surface morphology before and after adsorption of MO.

Fourier-transformed infrared spectrophotometer (Nicolet AVATAR 380) was also employed to analyze the surface functional of the OPEFB and surfactant-modified (1% CTAB-OPEFB) adsorbent. The potassium bromide (KBr) was used in the ratio of 1:100 (sample to KBr weight ratio) with oven-dried sample to make pellets at a pressure of 10342.13 kPa for infrared analysis. The spectra were recorded by 64 scan with 4 cm^{-1} resolution in the mid-infrared region.

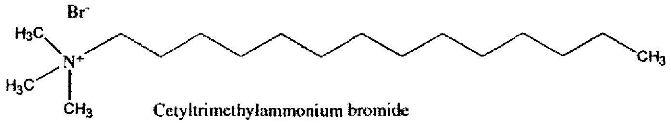
The point of zero charge of OPEFB and 1% CTAB-OPEFB was determined using the method described in a study by Fiol and Villaescusa [13]. Suspensions of 6 g/L of the sample were put in contact with 0.03 M KNO_3 solutions adjusted at pH values of 2.04, 3.01, 4.06, 5.56, 7.6, 8.5, 9.3, and 10.4. The suspensions were agitated for 24 h in an orbital thermostat shaker (Protech, Model: 903) at 100 rpm. The change of pH (ΔpH) during equilibration was calculated. The pHzpc was the trough of the pH vs. |ΔpH| plot. The pHzpc of an adsorbent is an important characteristic that determines the pH at which the adsorbent surface has net electrical neutrality. At this value, the acidic or basic functional groups no longer contribute to the pH of the solution.

About 0.100 ± 0.0001 g of weighed amount of sample was taken into Erlenmeyer flask before 20 mL of 0.1 M NaCl solution was added as background electrolyte solution. Then, 1 mL of either 0.1 M HCl or 0.1 M NaOH solution was added to change the pH of the OPEFB sample and 0.1 M NaCl mixture. The flask was left for agitation at room temperature to attain the equilibrium level. The change in pH during attaining equilibrium was converted into proton-binding capacity (Q) (mmol/g) of the OPEFB sample using the following equation:

$$Q = \frac{(V_0 - V_t)}{m}([H]_i - [OH]_i - [H]_e + [OH]_e) \quad (1)$$

where V_0 and V_t are the volumes (mL) of background electrolyte (0.1 M NaCl) and the titrant (0.1 M NaOH or 0.1 M HCl) added and m is the mass of adsorbent (g). Substituents i and e refer to the initial and equilibrium concentration.

Boehm titration method was used to determine the number of oxygen surface functional group in the activated carbon. About 0.5 g of OPEFB sample was placed in conical flasks with 50 mL of following solutions: 0.1 M of sodium hydroxide, 0.1 M of hydrochloric acid, 0.1 M of sodium bicarbonate, and 0.05 M of sodium carbonate. The capped conical flasks were sealed with film and stirred for 24 h and filtered, after that 10 mL of each filtrate was titrated with HCl and NaOH depending upon the nature of titrant. The number of acidic sites of various types was calculated



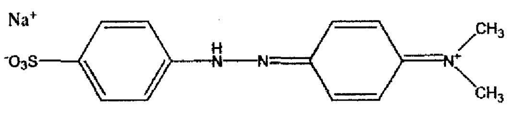
Scheme 1. Chemical structure of CTAB.

by presuming that sodium hydroxide neutralizes carboxylic, phenolic, and lactonic groups; sodium carbonate neutralizes carboxylic and lactonic groups; and sodium bicarbonate neutralizes only carboxylic groups. The number of basic sites was estimated by the amount of hydrochloric acid consumed by the carbon during stirring.

A modified method based on Boehm's technique was used to measure the cationexchange capacity (CEC) of the OPEFB samples. A weighed amount of sample (0.200 ± 0.0027 g) was placed into an Erlenmeyer flask. A volume of 50 mL of 0.1 M sodium hydroxide, 0.05 M sodium carbonate, and 0.1 M sodium hydrogen carbonate solutions was added. To attain equilibrium, the flasks were shaken for 24 h. After equilibration, the NaOH concentration was measured by titration with HCl. The quantity of NaOH consumed was converted to CEC and expressed in mmol/g using the following equation.

$$\mathrm{CEC} = \frac{(N_1 - N_2) \cdot V}{m} \tag{2}$$

OPEFB and 2% CTAB-OPEFB) masses of 0.1, 0.2, 0.3,



Methyl orange dye molecule in acidic solution

Scheme 2. Chemical structure of methyl orange dye in aqueous solution.

0.5, 0.7, 0.9, 1.0, and 1.5 g were taken separately for each percentage. The experiments were performed by adding the known weights of each adsorbent of 0.5% CTAB-OPEFB, 1% CTAB-OPEFB, and 2% CTAB-OPEFB into eight 250-mL capped conical flasks separately containing 50 mL of 100 ppm MO solution. For observing effect of temperature on adsorption, 0.7 g of 1% CTAB-OPEFB was kept in contact with 50 mL of 100 ppm MO dye solution at temperatures, ranging from 298 to 338 K in the temperature-controlled water bath. For observing the effect of initial concentration on adsorption, 0.7 g of 1% CTAB-OPEFB was kept in contact with 50 mL of MO dye solution with concentrations, ranging from 50 to 200 ppm at a fixed temperature of 298 K and pH of 6.3 inside a temperature control water bath. The conical flasks were shaken at 150 rpm for 24 h, and the equilibrium concentration of MO remaining in the solution phase was analyzed by UV–vis spectrophotometer (Shimadzu model UVmini 1240) at wavelength 464 Å.

The percentage of MO adsorption and adsorption capacity at equilibrium, q_e, of the adsorbents was computed using below equations:

$$\chi^2 = \sum \frac{(q_t - q_{t(\mathrm{mod})})}{q_{t(\mathrm{mod})}} \tag{5}$$

3. Results and discussion

3.1. *Characterization results of CTAB-modified OPEFB*

The effect of percentage of surfactant that used to modify the OPEFB surface was studied in this work.

The surfactant percentage was taken 0.5, 1.0, and 2.0% onto dry weight of OPEFB. The obtained 0.5% CTAB-OPEFB, 1% CTAB-OPEFB, and 2% CTAB-OPEFB were evaluated for the effect of percentage surfactant on efficiency of adsorption. Fig. 1 shows the removal of MO by 0.5% CTAB-OPEFB, 1% CTAB-OPEFB, and 2% CTAB-OPEFB as well as OPEFB. The dosages of adsorbents were taken in the range of 0.1–0.7 g with initial concentration of 100 mg/L of MO dye solution. The adsorption experiments were conducted at temperature 298 K. No significant amount of dye was removed by pristine OPEFB as can be seen in Fig. 1. The adsorbents (OPEFB) modified with different percentage of surfactant (CTAB) as mentioned previously were also investigated for adsorption of MO. It was observed that with the rise of percentage of surfactant onto the OPEFB, the adsorption capacity increases, from 0.5 to 1% much rise was observed, but from 1 to 2% only small rise in adsorption capacity was observed. Based on the experiments, it could be concluded that at 1% surfactant (CTAB), dose was sufficient for the saturation of surfactant on the surface of OPEFB. In view of these findings, 1% CTAB-OPEFB was selected as optimized adsorbent for further study.

Fig. 2 illustrates the FESEM micrographs of OPEFB adsorbents before and after CTAB treatment. After 1% remains and there was not much morphological change in the surface image as can be seen in figure (Fig. 2). The EDS studies of OPEFB and 1% CTAB-modified OPEFB are shown in Fig. 3. After CTAB treatment, the percentage carbon on the surface of adsorbent increased from 49.7 to 52.3%.

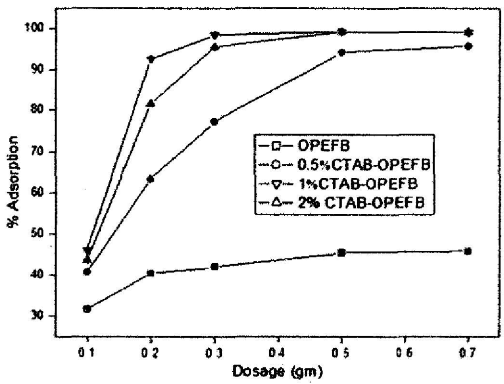


Fig. 1. Effect of adsorbent dosage for the adsorption of MO on different % CTAB-modified OPEFB.

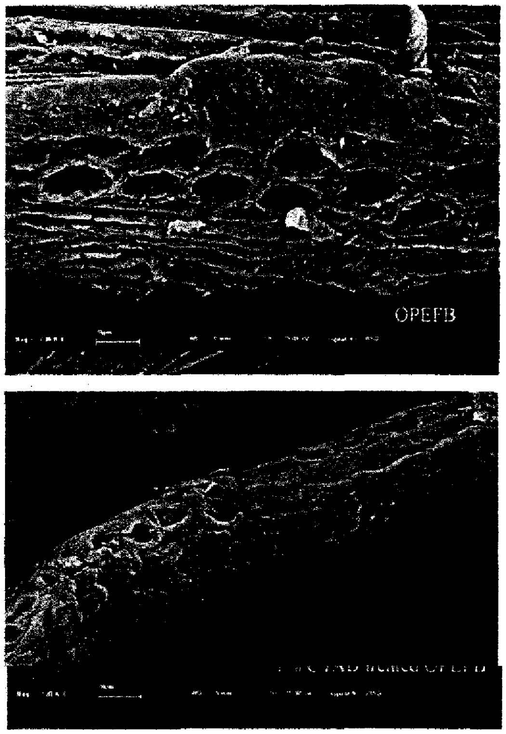


Fig. 2. FESEM micrographs of OPEFB and 1% CTAB-OPEFB.

The FTIR spectra of the samples as well as starting materials are shown in Fig. 4, and the spectra compare the presence of functional groups in parent materials, OPEFB and CTAB, and after combination of these two kinds of materials, the resultant change in functional groups occurs at the surface of adsorbent (1% CTAB-OPEFB). It can be seen from the spectra that multiple peaks are exhibited by the samples that indicate the presence of long molecular chains in the samples. For OPEFB and 1% CTAB-OPEFB, there is no major change in the number of peaks, because the major part of adsorbent (1% CTAB-OPEFB) contains OPEFB, and only 1% CTAB is present in it. Therefore, only minor broadening of the peak was observed. But this minor change in the surface functional groups plays a major role in MO adsorption. The Fourier-transformed infrared measurement for the 1% CTAB-OPEFB showed the presence of following functional groups: –OH (broad peak at 3,419, 3,570–3,200 cm^{-1}), methylene

0.448 mmol/g, respectively, compare to pristine OPEFB (carboxylic group 0.181 mmol/g and Lectonic group 0.868 mmol/g). The adsorption kinetics studies of MO on 1% CTAB-OPEFB proved that pseudo-second order was a suitable kinetic model. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption capacity of MO onto 1% CTAB-OPEFB with adsorption capacity of 18.08 mg/g. Thermodynamic parameters, enthalpy change, entropy change, and Gibbs free energy change were also calculated for the removal of MO. These parameters showed that adsorption on the surface of 1% CTAB-OPEFB were feasible, spontaneous, and endothermic in nature. The mechanism of the adsorption was ion exchange in nature.

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K_{eq} — chemical equilibrium constant
B_1 — Temkin isotherm constant
K_T — maximum binding energy
b — heat of adsorption
ΔG° — standard Gibbs free energy (J/mol)
ΔS° — standard change in entropy (J/K/mol)
ΔH° — standard change in enthalpy (J/mol)
t — time in minute
k_1 — pseudo-first-order kinetics rate constant (1/min.)
k_2 — pseudo-second-order kinetics rate constant (g/mg/min)
h — initial sorption rate (mg/g/min)
k_d — intra-particle diffusion rate constant (mg/g/min$^{1/2}$)
k_{d1} — first layer diffusion rate constant (mg/g/min$^{1/2}$)
k_{d2} — second layer diffusion rate constant (mg/g/min$^{1/2}$)
Q — proton-binding capacity (mmol/g)
V_0 — volume of background electrolyte (mL)
V_t — volume of the titrant (0.1 M NaOH or 0.1 M HCl) (mL)
m — mass of the adsorbent (g)
$[H]_i$ — initial hydronium ion concentration (mol/L)
$[OH]_i$ — initial hydroxyl ion concentration (mol/L)
$[H]_e$ — hydronium ion concentration at equilibrium

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Augmentation of EFB Fiber Web by Nano-Scale Fibrous Elements

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Keywords: EFB, nano-fibrils, fines, thin layer nano-fiber web, TN-webs.

Abstract. Treatment of the abundant oil palm empty fruit bunches with alkaline peroxide chemicals and subsequent fibrillation at varying mechanical energies resulted in favourable morphological changes of the generated fibers. The produced fibrous mass composed of intensely fibrillated elements ranging from micro to nano-diameter fibrils. Nano fibrils and webs of nano-fibrils were factors contributing to the functionality of the fibrous mass as fibre web augmentation elements. Profound improvement in fiber network is particularly attributable to the ability of the collected elements to fill up inter-fiber gaps and this was attributable to the micro elements in the form of micro fines, segmented micro-fibrils and webs of nano-fibrils. The uniquely generated thin layers of nano-fibril webs (TN-webs), were found to increase fiber web density by gluing multiple layers of fibers, together. Having landed on the surface of micro-fiber web, these TN-webs were identified as responsible for the masking effects of the underlying micro-fibres. Under such condition, fibers were observed to 'coalesce', suggesting also an augmented fiber network as evident from the 130% increase in tensile index and a 450% enhancement in burst index of the resultant fiber web relative to those formed with the basic alkaline peroxide chemical-mechanical refining (CMR) synergy. This reveals a great promise to EFB for application as super-strong fibre-web materials such as packaging and specialty paper-based products.

Introduction

Commensurate with Malaysia's long history of good environmental waste and effluent management [1], the once dross of the palm oil milling activities has been an acclaimed wealth factor, recently. Pulp-based packaging industry, for instance, announced a 63% savings on the capital for raw materials on switching to the use of fibrous mass from the oil palm empty fruit bunches (EFB) as the fibre source [2]. In fact, more applications from the research pipeline are projected for the sheer 20 mtpa EFB. Famed for wealth factor, the so-called 'green gold'[2] continues to prompt works on its functionality through minimal processing and conversion to pollutant sorbents [3-5] to the practical possibility of improved bio-fuel production [6]. Beyond research, a small amount of EFB is already in use as medium-density fibreboard, mats, mattresses, cushions and light furniture. It is also compressed as briquettes [7] and incinerated for electricity generation [2, 7]. Destruction of EFB lignocelluloses matrix allows production of siliceous melt enabling glazing of ceramics and pottery [8]. On the contrasting consideration, EFB, having predominance of cellulose, lower level of lignin in comparison to most local wood and having unique fibre characteristics, show better viability as raw material for pulping and conversion to paper-based products [9-11] as compared to bio-energy [11] and glazing applications. Besides the fibres as target yield, the waste constituting the loss in a typical fibre extraction process was also matchable to certain utilisation [12]. This, in turn, shifts the fibre industry closer to the zero-waste possibility.

From biomass utilization perspective, per hectare palm oil plantation could generate EFB pulp at least double the per annum pulp possibly harvested from the local rainforest. This corresponds to over 88 million trees-saving, on the assumption that all of the domestic EFB could be converted to pulp [7]. An economic way of doing this was attempted by applying an environmentally benign [8] and high-yield process concept of fibre extraction procedure, which was the breed of a alkaline peroxide mechanical pulping, APMP^{TM}, system reported by Cort and Bohn [13]. Within the system, the alkaline peroxide is an agent driving the swelling, softening and brightening of biomass and a subsequent mechanical fibrillation assist in the liberation of cellulosic fibrous mass. Being sulfur- and chlorine-free, the technique incorporates fiber extraction and bleaching in a single process or short segments of batch processes, thus, eliminating the need for a separate bleach plant, analogous to the acclaimed simplicity, flexibility and adaptability of the APMP^{TM} system [13-17].

Early attempts of scrutinizing EFB responses to alkaline peroxide [8, 9, 18] observed the wide possibility of fibre web quality by adjustments of experimental parameters and machinery. The results of synergizing a fixed level of the alkaline peroxide with variable mechanical refining energies (in short, CMR synergy) in the process of extracting fibers from EFB is hereby discussed from the light of fiber web strength augmentation. The huge polarity in fiber morphology and fiber web strength foresees a favourable outcome for high-end utilization of EFB.

Method

Materials. The fibrous strands of EFB from Sabutek (Malaysia) Sdn. Bhd were washed and air-dried. The vascular bundle strands were ground to about 500 μm particles collected on 200-mesh screen (R200) using Retsch AS200 sieve and shaker. These particles were soaked in distilled water at 70°C for 30 minutes in water bath and pressed at 103 kPa pressure to be 50% extractive-free.

Fibre Extraction and Fibrillation. Alkaline Peroxide Pulping (APP) of EFB was carried out by submerging EFB in alkaline peroxide at 10-to-1 liquor-to-EFB for 30 minutes to reduce the chances of leachate redeposition [9] onto EFB surface. The alkaline peroxide containing 4% sodium hydroxide (NaOH) and 4.5% hydrogen peroxide (H_2O_2) was reacted with EFB for 30 minutes at 70°C and ambient pressure to soften and brighten the biomass. The AP-treated biomass was next refined using Sprout-Bauer 12" single disc refiner with 54.95 kWh/t specific refining energy for 4% pulp consistency and refining temperature of 33.5°C. The aforementioned condition is denoted as the basic alkaline peroxide chemical-mechanical fibrillation (CMR) synergy. Part of these fibres were subjected to further refining in the 1-20 kWh/mt energy range. CSF values were acquired in accordance to TAPPI Test Method T 227 om-99 [19], made into handsheet and examined for their web strength by selected mechanical testing (tensile, tear and burst) in T 227 om-99.

Microscopy and Fiber Analysis. Gold-coated fibre web and fibre smear were examined qualitatively using Carl Zeiss Leo Supra 50VP scanning electron microscope (SEM). Fibre dimensional characteristics and by-size fractions were acquired from Sherwood FAS-3000 Fiber Analysis System (USA), and this analysis was performed on pulp suspensions as recommended by the instrument manufacturer.

Results and Discussion

Dimensional Analysis of Fiber Fractions. Under the lowest possible alkaline peroxide chemical-mechanical refining (CMR) synergy, an APP process was reported as consisting of fibre bundles, vessel elements, fibers and fibrillated vessel elements [12]. Heightening of the CMR synergy by increasing the mechanical fibrillation energy (while keeping the alkaline peroxide at fixed level) resulted in further shearing and cutting of the fibrous mass and this is depicted on the CSF values in Table 1.

Table 1, Canadian Standard Freeness of EFB Fibres by Fibrillation Energies

	Fibrous Mass by Fibrillation Energy				
	0 kWh/mt	1.7 kWh/mt	5.0 kWh/mt	8.3 kWh/mt	17.0 kWh/mt
Web Name:	(FM0)	FM1	FM2	FM3	FM4
CSF (ml)	495	372	133	76	57
Relative %		-25%	-64%	-43%	-25%
Relative to FM0	0	-25%	-73%	-84%	-88%

NB: Basic CMR Synergy ≡ 0 kWh/t

From 1.7 kWh/mt to 17 kWh/mt, reduction in long-fibre counts is followed by an increment in the proportion of fines for a total of 139%, which corresponds to a gradual drop of 25%, 73%, 84% and 88% in the CSF relative to the native APP fibres (FM0, Table 1). This further reflects the aforementioned vast increase in fines contents and in turn, an increase in surface area for hydrogen bonding between water and fiber. Besides fines, internal and external fibrillation of fibres had increased exposure of the internal fibre structures and these also provide areas of contact with water, besides increasing the possibility of such entanglement as in Fig 1.

Fiber length of the fibrous mass decreased with an increase in fibrillation energy (Table 2) due to the anticipated severe shortening of fibers arising from continuous mechanical shearing force. Only meagre counts of long fiber constituted the fibres mass while a relatively more uniform count of medium, short and fines fiber were obtained. From handling perspective, the extremely low CSF value of FM4, therefore, increases the probability of water-fiber bonding and the resultant poor drainability and this could be a serious obstacle in papermaking line due to the tendency of fines to agglomerate and block the papermaking screen. These materials, however, may intrinsically improve paper web strength, analogous to the effects reported by Kamaluddin and team [12].

Table 2, Dimensional Fraction (%) of Fibres and Fines

Dimension		Fraction Name	Fibrous Mass by Dimensional Fractions (%)				
Width (μm)	Length (mm)		FM0	FM1	FM2	FM3	FM3
< 3-60	< 0.11	Fines	14.1	15.1	14.4	24.9	33.7
				+7%	-5%	+73%	+35%
3-60;	0.11-0.45	Short	21.6	25.6	31.7	32.9	35.1
				+19%	+24%	+3.8%	+7%
3-60	0.56-1.46	Medium	50.1	50.0	48.8	40.9	30.5
				-0.2%	-2%	-16%	-25%
3-60	1.57-7.17	Long	11.3	6.6	3.9	1.2	0.6
				-42%	-41%	-69%	-50%

Fibre length ranging from 0.125-0.250 mm is ideal [20] for intense fiber-to-fiber bonding. In this regard, long structures such as split vessels are liable for the interruption of fiber-fiber bonding due to the risk of entanglement or agglomeration, which adds the count of over-sized structures [20]. The favoured hydrogen bonding of the obtained pulp results in good mechanical strengths (Fig. 2). The more often fluffy (Fig 1a), rather than linear structures (Fig. 1c) provide bonding sites besides by filling snugly into the fibre web micro-voids.

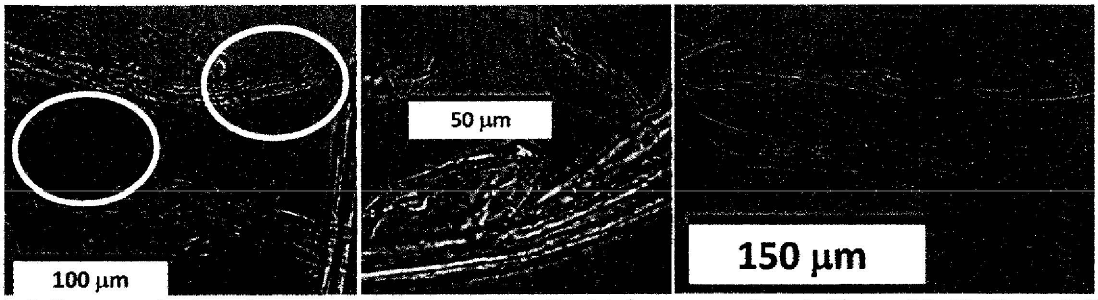

Fig. 1, Micrograph showing entanglement of fibrils (a) broom-end and fibers (b) fibrils and fibrils (c) less entanglement amongst linear fibrils.

Mechanical Properties. A maximum of 5 kWh/mt mechanical fibrillation produced the desired external fibrillation of the commonly encountered fibre bundles as portrayed by FM1 and FM2. Predominance of medium-size fibrous mass (Table 2) resulted in the increasing tensile and burst indices (Fig. 2) due to the availability of fibres offering good possibility of hydrogen bonding. This is also rendered by the high relative abundance of the long fibres.

Shortening of fibrillated vessel elements resulted in gradual predominance of short-fibers starting from FM3 where 8.3 kWh/mt energy was applied. These short fibers offered no more hydrogen bonding sites per fiber and show no further increase in tensile strength of the fiber network (Fig. 2a) as web's ability to withstand the pulling force till the point of brittle failure depend not only on fibre bonding, but also fibre length and, to a less extent, fiber strength. The web formed by bonding promoted by the shorter fibrous mass, moreover, showed resistance to burst impact with an increase in fibrillation energy (Fig 2b). This is attributable to the positive gluing effects of fibrils and thin fibril webs (Fig. 3b), which had ultimately diminished micro-void and web porosity. This extensive adhesion between fines-fiber and fines-fines leading to high fiber packing is portrayed in Fig. 4c. Uniquely, the generated fines serve more as natural filler of micro-voids, which is typical of alkaline peroxide EFB fibre network. These fillers reduce the possibility of fibers being pulled out of the paper plane, resist air flow and thus, enhancing pulp network resistance to burst impact.

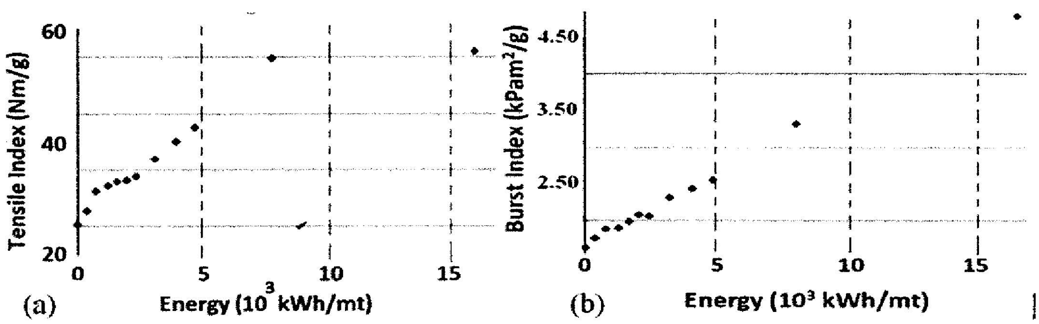

Fig. 2, Mechanical strengths of fiber web a) tensile index ($0.4<\sigma<3.5$) and (b) burst index ($0.1<\sigma<0.5$) of papers produced from the EFB pulp.

Fibre Web Microscopy. With the common mass of 200 μm to 1000 μm fibres (Table 2) in FM0 less of fines flogs are winessed in Fig 3a (right) as compared to the more glaring evidence of sub-micron fibrils dangling on the fibrillated fibers (Fig 3b, right). The transition in the extent of fibrillation of the fibre surface resulted in the dodgy appearance of fibre web by the intensely fibrillated fibers (Fig 3b cf. Fig. 3a). Besides the dodging effect, the web of fibrils had also rendered the aforesaid gluing effect, evident from the enhanced mechanical strength of the fibrillated-fibre web. The friction forces of fibrillation process had also led to the formation of an extremely thin fibrous sheets (Fig. 3c). Higher magnification of these sheets shows vast amount of threads of nano-fibrils (Fig. 3c – far right). Apart from filling up internal voids, these are also likely to land on the surface of the fibre web, giving the coalescence appearance. Specifically in the case of FM4, well-defined fibers are evidently masked on the web surface (Fig. 3c – far left). Apart from that, the nano-fibrous construction is also believed to impose the overall translucence effect of the associated fiber web sheets. In their presence, there are higher chances of nano-voids being filled up, resulting in an apparently condensed fibre web and thus, high sheet density.

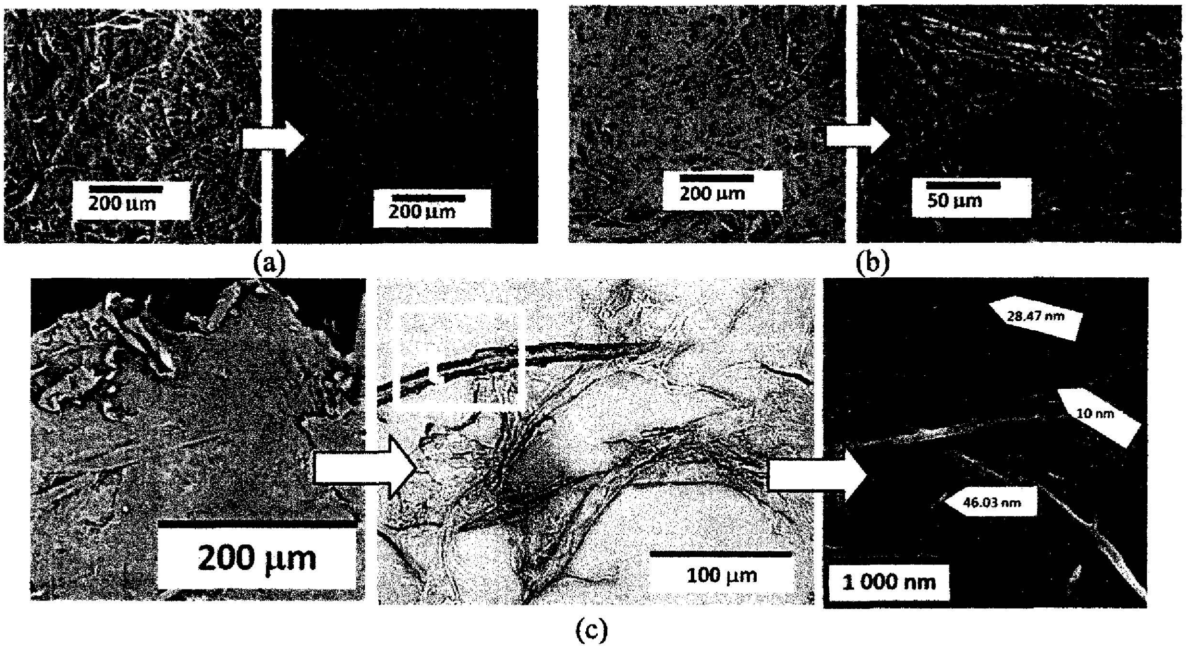

Fig. 3, Fiber web surface and the associated fiber suspension for (a) basic (0 kWh/mt) and (b) 1.7 kWh/mt and (c) 17 kWh/mt CMR synergies. An additional micrograph on the right for (c) shows evidence of nanofibre network.

Conclusion

The applied mechanical fibrillation energies offered a huge polarity of pulp qualities, apparent from the 130% and 450% possible increase in tensile and burst indices, comparing the web of fibers from basic CMR synergy to the applied maximum fibrillation energy. This is attributable to the tremendous increase in bonding sites and filling of voids by sub-micron fibers and thin layers of nano-fibril webs (TN-webs). The overall findings demonstrate the possible fiber web augmentation by nano-web elements by their intrinsic gluing and packing properties Although moderate in compensating with the sacrificed fiber strength and length, these elements manifest more possibility of exploiting EFB in higher end pulp-based products development.

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Augmentation of EFB Fiber Web by Nano-Scale Fibrous Elements

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EFB Nano Fibrous Cells for Paper Smoothing and Improved Printability

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Keywords: EFB, nano-fibrils, nano-cells, smoothness, printability

Abstract. Nano-fibrillation of the oil palm empty fruit bunches, EFB, by synergizing the alkaline peroxide chemicals and a subsequent refining process was found to liberate useful fibrous mass. Of these, the nano-fiber web materials were found to render smoothing effect by covering the trough between bound fibers and thus, hiding the true morphology of fibers on the paper surface. Apart from smoothing, which is one of the important paper properties requiring expensive furnishing, the thin nano-fiber webs (tn-webs) also held the paper structure firmly by plunging of the nano-fibers into the gaps between the micro-fibers. This is mainly due to their dimensional (10 nm < Diameter < 100 nm) compatibility. The smorgasbord shapes of the liberated tn-webs have a relatively lighter structures, found in the range of 2400-121500 μm^2 areas, could be abundantly produced by adjustment of refiner blade type with a specific alkaline peroxide chemical level. The maximal level of paper smoothness was measured by the laser toner spread (fusion or otherwise). Analysis reveals more extensive toner fusion on Waldron-4 sample, suggesting surface uniformity anfd better leveling of fibers on paper surface. It turns out that, this corresponds to the fibers detected with more evidence of delamination and thus, more count of nano-fiber web. Not only is this a proof of correlation of nano-fiber web intensity with paper smoothness but also a possible promise for an alternative measure for paper printability enhancement.

Introduction

Paper values increase with good printability and an improvement in printing technology may to an extent contribute to the average demand growth rate of 2.8% per annum [1]. Catering for the demands must come with concerns over the environment. Thus, in countering the controversial use of wood and deforestation, attempts were made at extracting papermaking fibers and fillers from an abundant oil palm residue, the Empty Fruit Bunches, EFB.

Today, EFB fibers are commercially used as economic fiber source in the packaging industry. Pulp-based packaging industry, for instance, announced a 63% savings on the capital for raw materials on switching from wood-based imported fibers to the use of fibrous mass from EFB [2]. In fact, more applications from the research pipeline are projected for the sheer 20 mtpa EFB. Beyond packaging works that has famed EFB as a wealth factor, the fibers are also found suitable for newsprint and printing grade products. Printability by one definition [3] or the other, then, becomes one of the deciding competency factors.

Selective views pointed that printability is associated with paper smoothness. Not with unanimous agreement, smoothness is said as having close association with surface gloss [4]. These combined facts are inferred from the works of Kauppi and team [5]. Despite the discrepancy in views, however, gloss has been an acceptable measure of paper smoothness in the pulp and paper industry. On the basis that an ideal surface should catch and reflect the light, increasing the void volume should decrease the index of refraction and thus the gloss [4].

This study examines the printability of papers produced from EFB by scanning electron microscopy to rule-out the previously reported limitations from conventional gloss measurements. Several modes of sample preparation/sample mounting had given meaningful information about the morphological features of fibers associated to the paper web. This study identifies the forms of EFB fibers responsible for good printability and paper smoothness.

Experimental Procedure

Conversion of EFB Vascular Bundles to Fibers. The vascular bundles of EFB were obtained in the form of bales. These were loosened, washed thoroughly and air-dried before grinding to 500-micron particles. Dewaxing was done by soaking the biomass particles in distilled water at 70°C for 30 minutes and press at 15 psi for removal of 50% of extractive components. On these, alkaline peroxide (AP) pre-mixture of 2:2.5% hydrogen peroxide to sodium hydroxide was allowed to react for 40 minutes at 70°C and then pressed to remove about 80% of the liquor. To initiate more powerful fibrillated mass, the alkaline peroxide impregnation (API) stage was repeated two to four times on the same EFB mass. The AP treated mass was then refined with Andritz Sprout Refiners of two blade variations 12716 and D2A505 and fiber webs or papers made from the generated fibers are denoted Bauer and Waldron, respectively. Both refiners are configured with 12-inches double-disc blades with single rotating disc.

Fibre Morphology. The obtained fibers were made into hand sheets in accordance to TAPPI Test Methods 1996-1997 [6]. While light microscope model Olympus BX41 was used to analyse isolated fibers on a slide of thin smears of fibers, the morphology of paper webs were observed under Leo Supra, 50 VP Carl Zeiss Scanning Electron Micrograph. The samples were placed on a stub using double-sided electrically conducting carbon adhesive tapes and then gold coated using Polaron Equipment Limited model E500 with a voltage of 1.2kV and 20 Pa for 10 minutes.

Printability Test. Laser jet printer was used to print lines at the same location on the produced papers. It is important to print the surface at once (< 30 seconds lag) in order to avoid the possible time effect on ink stability [7,8]. The ink or toner does not permeate the substrate, as does conventional ink, but forms a thin layer on the surface by adhesion to the paper surface prompted by using a fuser fluid with heat process (toner). Printed areas were observed under Dinolite portable microscope and printability was evaluated by the count of completely printed 2 mm x 2 mm grid. This was done by magnifying the 50 mm x 50 mm printing areas and superimposing with the transparent film of grid. Calculated as percentage of printed grids, printability values were derived from equation 1:

$$\text{Printability} = [(\text{Printed grid}) / \text{Total grid}] \times 100 \quad (1)$$

Results and Discussion

Paper printed with straight lines was examined under several versions of microscopes and Fig 1 presents the magnified view of toner distribution on fibers associated with the two produced papers. Enormous unprinted areas are apparent on Bauer paper surface and this corresponds to the paper made from EFB fibers refined in Andritz Sprout Bauer refiner. Fiber shapes are also apparent and variable. The failure of ink to adhere was due to the presence of gaps (Fig 1d) occurring as a result of un-closely bound fibers or fiber packing and this is governed by fiber size, flexibility and conformability. Detailed elaboration of this can be based on the principles of laser printing in Fig. 2.

Laser printing works by the attraction of opposite charges. As the printer reads data from the computer, the image processor converts it into an image. While the image is being stored for printing, the photoconductive drum (Fig. 2) rolled and the surface is being charged by a high voltage corona wire (2). The rolling drum is then illuminated (3) by the laser beam that was converged by a complex mirrors and lenses system. The beam then 'draws' the image on the surface of the moving photosensitive drum surface and discharge the surface.

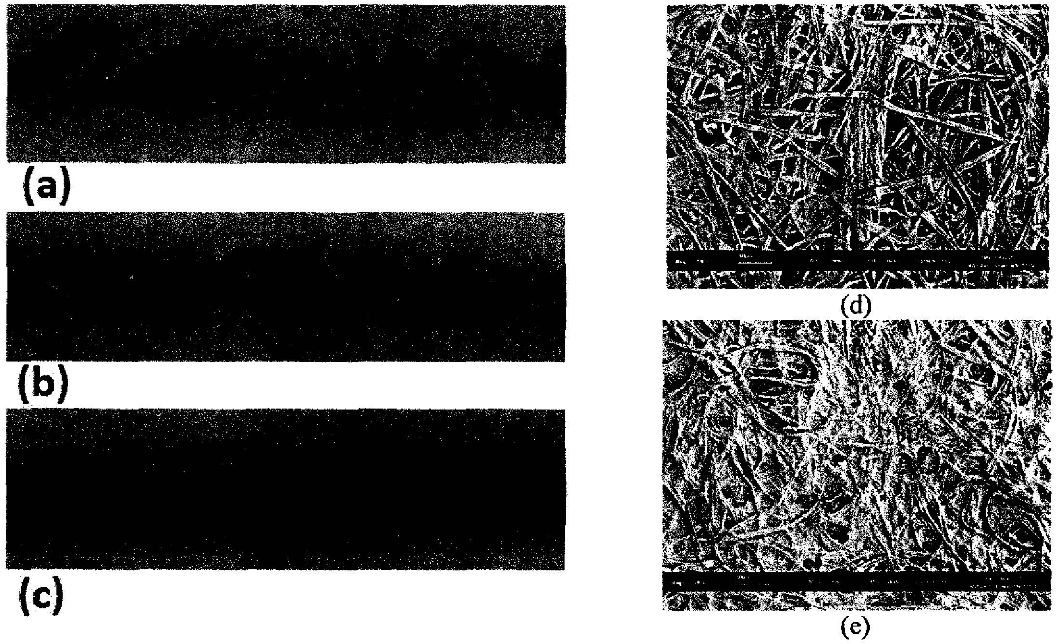

Fig. 1, Toner distribution on three papers (a) Bauer (b) Waldron and (c) commercial A4. Under x100 magnification (d) Bauer paper surface appears more porous while (e) Waldron paper showing much less gaps.

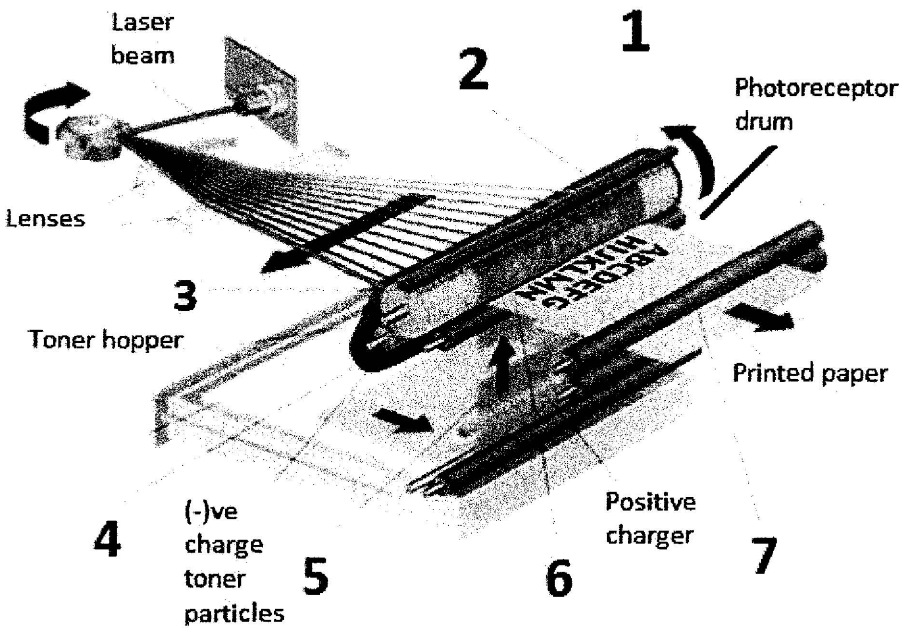

Fig 2, Laser printing parts [8].

Put simply, if the drum surface were initially positively charged, a net negative charge image is etched on the drum by wiping off positive charge. Once the entire image is drawn, the drum rolls further. Along the drum path, a toner developer is placed, which subjects the surface to come in contact with the positively charged toner particles made up of pigment and a plastic polymer (4). The toner-embedded drum then print the electrostatic image as it comes in contact with the negatively charged paper (5). Since like charges repel and unlike charges attract, only the negatively charged (image etched) region on the drum attracts the positively charged toner particles and so, as the paper surface comes in contact with the drum, only the positively charged toner particles stick to the paper (6), creating an exact image of the page. The printed paper is then passed through hot

Teflon coated rollers (7), which melt plastic in the toner particles to make it stick on the paper before rolling it out, warm [9].

As gaps on the printed region of the Bauer Paper did not show any sign of toner particle (Fig. 3), the main point of failure could be insufficient contact with the toner-embedded drum surface due to paper surface coarseness. Failure of toner fusion, which also stems from the inability of the paper to be in full contact with the hot Teflon coated rollers, which melt plastic in the toner particles, could also attribute to the lower (70%) printability (Table 1) and this is depicted on the micrograph of the paper sample (Fig. 1d).

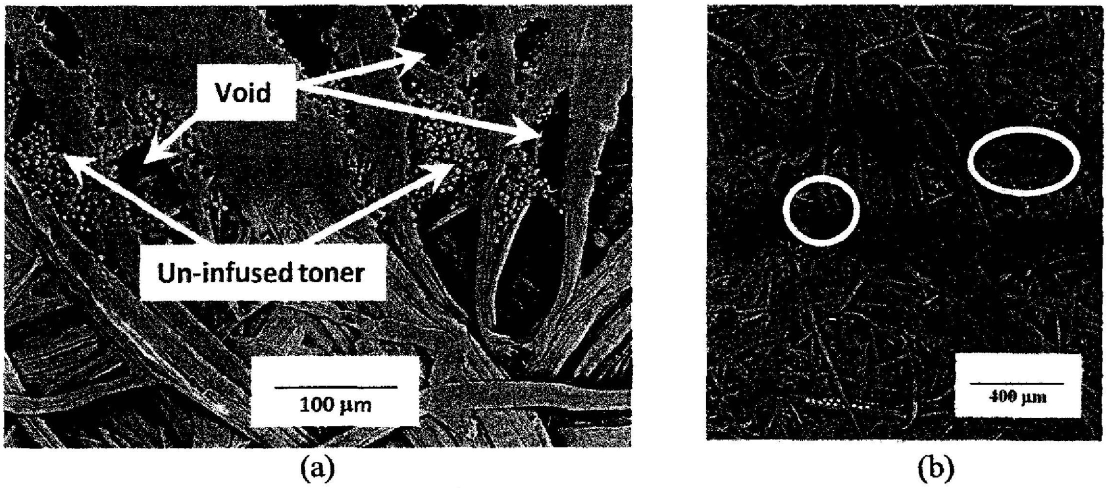

Fig. 3, Printed Bauer paper showing (a) close-up of voids and un-infused toner particles resulting in the (b) unprinted surface (circle).

Table 1, Comparative Data for Printability

Fibre Web Sample	Printability		Inferiority to Commercial A4	Relative Superiority
Bauer 1	79	70%	20%	-
Bauer 2	61			
Waldron 1	90	82%	7%	20% (cf. Bauer)
Waldron 2	73			
Commercial A4 1	100	88%	0	14% (cf. Bauer & Waldron)
Commercial A4 2	76			

Analysis of the fibrous mass for Bauer Paper indicates the presence of fiber bundles and segmented fiber bundles (Fig. 4). It was these structures that were responsible in the variable fiber sizes and interruption in inter-fiber bonding. Gaps or voids are the results of disconnection in inter-fiber bonds following the presence of over-sized fiber bundles. These were made especially apparent due to the absence of fiber webs arising from the delamination of fiber walls.

Fig. 4, Fiber bundles (left) and segmented fiber bundles (right) amongst pulp mass in Bauer paper.

Printing seems improved on Waldron surface with evidence of more densely packed fibers (Fig. 1e) of less size variability. Good packing also implies less gap or at least, shallower gaps (Fig.

5a and b). This corresponds to 82% printable surface, which is only 6% inferior to commercial A4 shown in Fig. 1c.

It is noteworthy that fibers of Waldron paper may also be composed of coarse fibers (Fig. 1e cf. Fig 5c) but these are masked by the 'coalescence' appearance of the liberated thin webs of nano-fibril (TN-webs) shown in Fig. 5e.

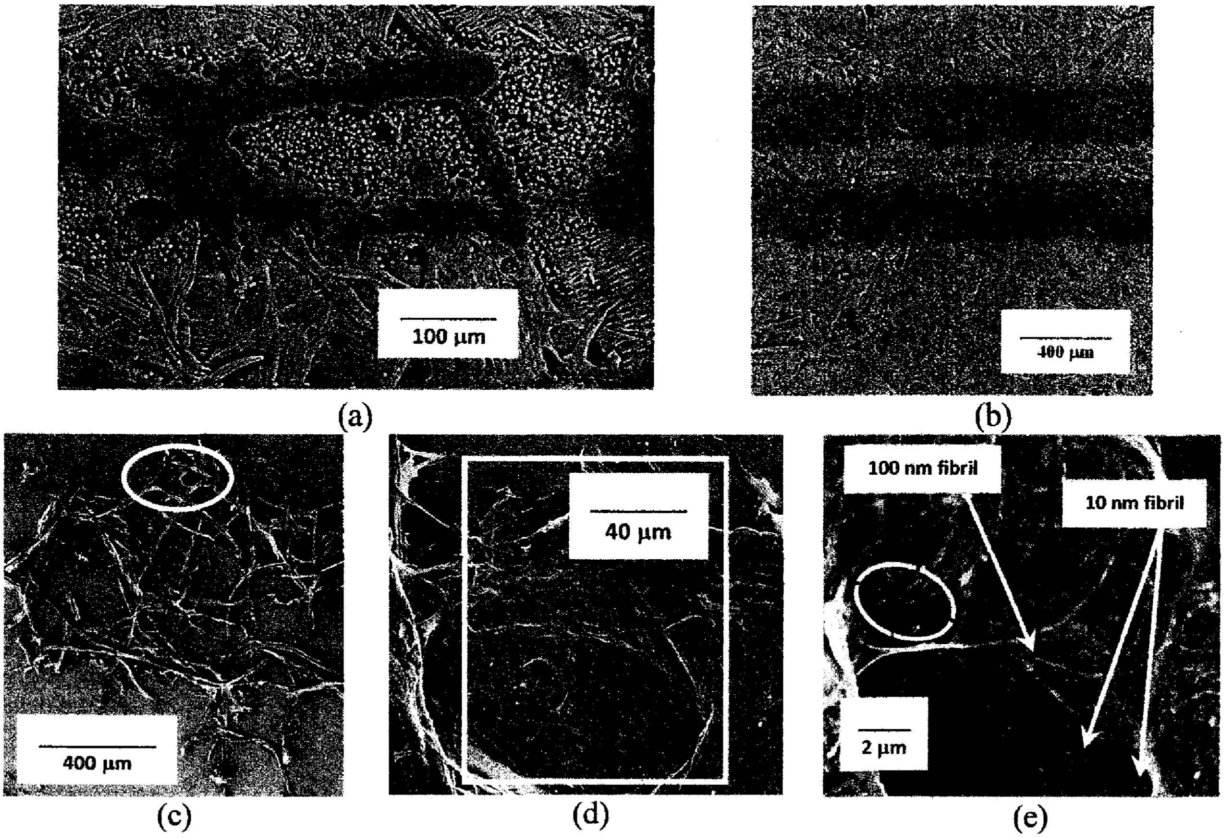

Fig. 5, Waldron paper with (a) shallower gaps and more (b) printed surface. The paper also contains (c) coarse fiber masked by (d) nano-fibrils web zoomed as (e). Oval indicates plunging of nano-fibils (10 nm < diameter < 100 nm) into gaps.

The key factors for the good printability of Waldron, therefore, lie entirely on the fiber characteristics. Uniform fiber sizes provides uniform inter-fiber bond network throughout the paper. Paper smoothness, on the other hand is rendered by the layering of the web of nano-fibrils, liberated as a result of delamination of fiber walls. This arises as a result of good alkaline peroxide impregnation into EFB mass, which forces the chemical into the biomass structure to react more effectively with the lignin that not only binds the cellulose fibrils together but also binds the inter-layers of nano-fibrils. As a result of subsequent shearing from the refining process, the loosened inter-layer bonding had liberated one or multiple layers of the nano-fibrils. This results in what was presented as delamination. Fiber web uniformity and good fiber packing of the examined paper was also the result of plunging of nano-fibrils (Oval in Fig. 5e). The correct synergy between the alkaline peroxide and the pressure for mechanical fibrillation, therefore affect paper web formation by the engendered smoothing effects from TN-webs. While the fiber in Bauer paper shows almost no evidence of liberated webs, Waldron paper consists of webs of 2400-121500 μm^2 (cf. the unliberated TN-webs of only 14-2541 μm^2 for Bauer papers) calculated as the total areas of a smorgasbord TN-webs, with an estimated thickness of 10 nm to 100 nm.

From surface chemistry point of view, the presence of nano-fibril webs provide a much larger surface areas of hydroxyl groups. Besides smoothing effects, which is commonly achieved in the papermaking industry by multiple coating layers [10] by the mechanism of hiding fibers [11], these also provide sites for charging and reception of the charged toner particles. This coincides with the claim that surface OH- groups render paper surface acid-base character and thus acts as good sizing agent [12, 13]. The fact that printability can be improved without addition of mineral filler or expensive calendering proves the resemblance of EFB nano-web for coating application to the trendy bridging of the gap between ecology and printability.

Conclusion

The delaminated cells of EFB are composed of nano-fibrils webs. These are the cells responsible for the smoothness of paper made from EFB fiber extracted by properly synergizing the effect of alkaline peroxide with mechanical refining. Paper smoothing by the nano-fibril webs was rendered by the abundant hydroxyl groups, which is the natural sizing agent. Smoothing of paper surface ensures good printability and this places paper from EFB fibers closer to commercial papers, in light of printability performance.

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Nanofibre Network Rooted from the Alkaline Peroxide Treatment of Oil Palm Empty Fruit Bunches

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Keywords: Biomass, EFB, nano-fibers, biomass, nano-elements.

Abstract. The increasing popularity of the oil palm empty fruit bunches (EFB) as a source of non-wood fibre has prompted a variety of research on processing and utilisation of the material. In an attempt to define the characters, reusability and end-of-life, oil palm EFB was processed by the alkaline peroxide variable treatment (APVT) systems. Low synergy between alkaline peroxide (AP) chemical and mechanical fibrillation through fibrillation (CMR synergy) revealed the yield of segments of EFB vascular bundles while heightening the mechanical forces further, generated more uniform but a mixture of fiber and segments of fibre bundles. An intermediate CMR synergy generated fibres forming a more well-defined but a rough resultant fibre network due to partial fibrillation of the vascular bundle. Applying maximal CMR synergy was found to generate higher yield of network strengthening fibrous cells. These were later identified as nano-scale fiber network or "nano-scan", consisting of 10-80 nm diameter fibers arranging themselves in a systematic network. Analysis of the polarity of fibers harvested from the APVT systems manifests the systematic construction of nano-fibrils winding in helical manner to form arrays of nano-fibres that glue themselves together as micro-fibrils. Interconnections between fibers and other gluing elements led to the vascular bundle known as the EFB biomass that was once dross and that can now be marvelled as an alternative source of nano-fibers for the nano-industry sector.

Introduction

Famed for strength factor of botanical structures [1], the abundant, renewable and biodegradable cellulose [2] fibers have long been recognised for their vast list of applications. While micro-fibers serve the common functions in the making of pulp-based products, nano-fibers define a new edge of fiber utilization. Driven by such key areas as electronics, energy, medicine, chemicals, coatings, catalysis [3] as well as textile and apparel [4], today, nano-fibers find dominant use in the mechanical and chemical industry, which accounts for more than half of the total market share [5]. The big impact of this sector is implied by a ten-fold increase in the production of nano-fibers in 2011, in comparison to that reported in 2002. Projecting an extended end-user market, the production volume in 2016 is conservatively estimated to reach more than 350 000 tonnes, with nano-cellulose and nano-fibres included in the tonnage [3]. The enormous growth is due to their unique properties such as large specific surface area, small pore size, high porosity and a smaller diameter size over the conventional fibers [5].

The expanding demand for nano-fiber and nano-cellulose prompts the need for an efficient nano-fiber production line with flavours of flexibility, cost effectiveness, speed and environmental compatibility. This is essential in ensuring an extra long-term sustainability of the supply regime. In line with this, the potential of the abundant residual materials such as the oil palm biomass for application in this sector is worth a study. Being one of the influential sectors to global GDP [6], the palm oil milling sector in Malaysia leaves approximately 20 mtpa of the fruit-free palm bunches known as the empty fruit bunches (EFB). The fibrous nature of the residue has now gained recognition as a wealth factor for the packaging industry. By switching from wood-based imported fibers to the use of EFB as source of fibers, for instance, a 63% saving on the capital for raw materials was proven achievable [7]. Beyond packaging works that has saluted EFB as profit-making item, high-end uses of the materials are also projectable in the advent of nano-technology infused with the idea of renewability and sustainability.

Commensurate with this, a study focusing on the fibrous contruction of the said popular local biomass was carried out. Beyond the conventional fibre, an eco-friendly [8] fibre extracting agent called the alkaline peroxide is used to liberate the finest possible nano-fibers. As fascinating fibers and cells could be obtained by adaptation to the various possibilities of alkaline peroxide chemical level and mechanical fibrillation [9-12] synergy, the system adopted for studying the ultra-structure of fibrous materials is denoted as an alkaline peroxide variable treatment or APVT system. This paper discusses the pathway for liberating and understanding the nano-fiber contrstruction in the EFB biomass.

Methodology

Pre-cleaning of EFB Biomass. The fibrous strands of EFB in the form of the dried long fibrous strands or vascular bundles were washed and air-dried indoor, ground to 500 μm particles or downsized to 2 cm segments. As a measure for removing the non-cellulosic materials, these were made 50% extractive-free by soaking the biomass in distilled water for 30 to 40 minutes at 70°C.

Tracking Delamination and Fibrillation of EFB. In this paper fibrillation is used to refer to the process of generating fibrils while delamination refers to the peeling out of the thin layer of nano-fibril web (TN-webs) or nano-scale elements (nano-scan) from the fiber or micro-fibril. It was identified that the synergy between the alkaline peroxide chemical and mechanical refining, AMR, which is also abbreviated as CMR for chemical-mechanical refining, can be synergised differently to initiate different extents of fibrillation. In alkaline peroxide various treatment (APVT) systems, the basic CMR synergy is referred to as an APMP system and a wide variation in refining mode was also attempted [9-12]. Table 1 provides the summary of CMR synergy in the adopted APVT system.

Table 1, Speciation of the APVT Systems

CMR Synergy ▾	API by Level (%) & Stages			Mechanical Refining Energy (kWh/t)		
	2:2.5%	4:5%	8:10%	M1: 10-60	M2: 10-60	M3: 12-80
Low CMR APMP	■			■		
High CMR APP	■■	■■	■■		■■	
APFI		■			■	■

NB: ■ Single alkaline peroxide impregnation (1-API) | ■■ Multiple-stage API

Fiber extraction via APVT systems were carried out on the cleaned and segmented or particle form of EFB. To observe segmented vascular bundles, APMP was carried out, which involved only low energy refining of the AP-treated EFB. By employing the most severe condition (APFI), diversified fibrous cells could be obtained and these were classified accordingly and stored for analysis.

Image Analysis. Light microscope model Olympus BX41 was used to analyse isolated fibers on slides. These were then observed under Leo Supra, 50 VP, Carl Zeiss Scanning Electron Micrograph by adhesion with double-sided electrically conducting carbon tapes and gold coated using Polaron Equipment Limited model E500 with a voltage of 1.2kV and 20 Pa for 10 minutes.

Results and Discussion

Oil palm empty fruit bunch vascular bundles (EFB), a monocot famed as *Elaise guineensis* amongst botanical scientists, is at origin brownish, attributable to the 5% redness, 19% yellowness and 20% vividness [12]. To naked eyes, the soft brown tone of the biomass imparts 64% lightness on CIELAB chromaticity scale, which corresponds to 13% ISO brightness [12]. From chemistry viewpoint, the colour factor of EFB is governed by the chromophoric materials from the extractives, lignin and transition metals. Upon reaction with alkaline peroxide, chromophoric groups are altered and a portion of these are released as auxochromic materials while a portion is retained as light lignin fragments (LLF). Despite retention of LLF, fibers derived from the APVT systems offer good photostability [13] with pleasant dose of eye-relaxing yellow tone.

The lignin modifying effects aided the liberation of fibers by lowering the capacity of the binding materials [14]. Physically, the swelling and softening of EFB lubricated shearing of the vascular bundles during mechanical refining (MR), which is aimed at freeing the fibrous mass. The thoroughness of this process is therefore decided by the extent of the alkaline peroxide chemical (C) penetration into EFB. Whether alkaline peroxide is present as residue or as fresh chemical, the chemical-mechanical refining (CMR) synergy is the key factor not only in liberating fiber but in attaining the target fiber morphology.

Beginning with the lowest-end of the APVT system, Fig. 1 presents the fibrous mass as blend of vascular bundle segments, fibre bundles and less of individual fibers. The poor alkaline peroxide reaction with EFB is apparent from the presence of intact silica and silica craters on the biomass structure as elsewhere [11] described. The presence of these segments resulted in low paper strength and coarse paper network (Fig. 1a) due to the non-uniformity of the fibre web structure. The low fiber network strength is also attributable to the interruption of fiber-to-fiber bonding. Evidence of segmented vessel elements (circle in Fig 1a) is an important factor to the poor inter-fiber bonding of paper. On paper web surface, these contribute to dustiness and poor printability. The close-up look at this structure (Fig. 2a) explains the aforementioned effects.

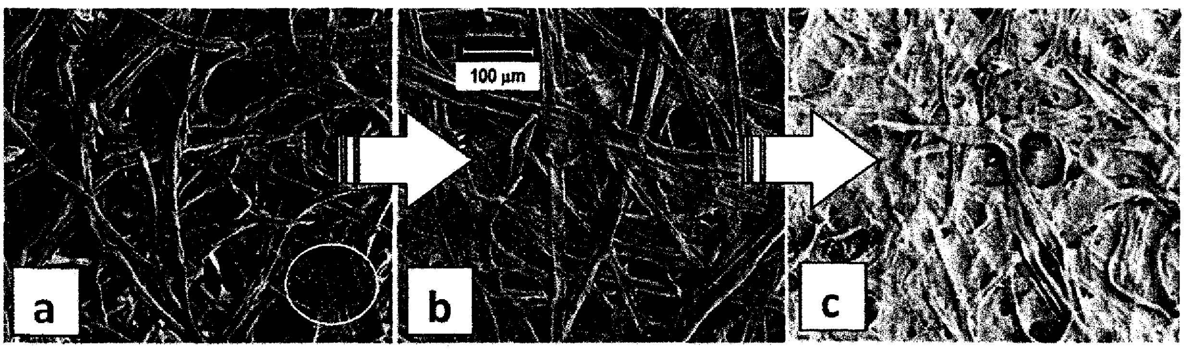

Fig. 1, Transition in thoroughness of EFB fibrillation via APVT systems (a) APMP, (b) APP and (c) APFI.

It appears, thus far, that raising the level of alkaline peroxide in APP had eased further fibrillation of the fibre bundles to yield more of the individual fibres. This is favourable in giving strength as well as aesthetic and kinaesthetic values to the fibre network (Fig. 1c), as a result of extensive fibrillation arising from the effective CMR synergy. The segmented vessel element from the APMP system (Fig. 2a) appeared severely delaminated into a layer of pitted structure (Fig. 2b) as a result of heightening the AP level and repeating the alkaline peroxide impregnation stages in the APP system. Such cell delamination is indeed a very likely occurrence in an APP system.

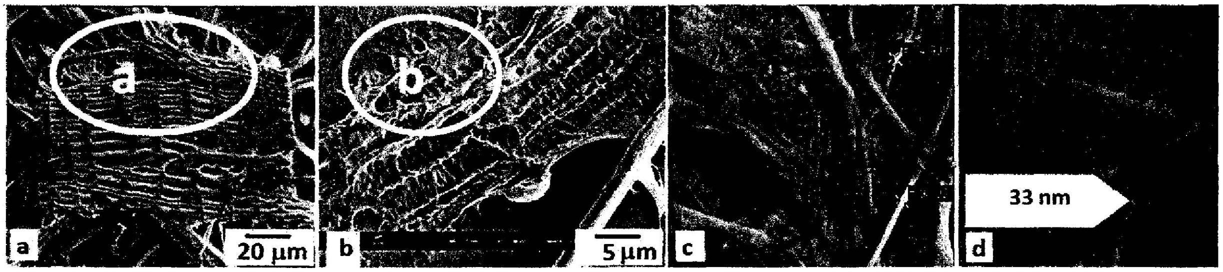

Fig. 2, Splitting and delamination of EFB vessel elements from an (a) APMP and (b) APP system with evidence of thin nano-fibril web (TN-webs) from APFI system showing (c) above 33 nm and (d) below 33 nm fibrils.

As a result of delamination in Fig. 2b, fibre strips are less apparent due to the presence of the masking cell layers. The overall paper or fibre web appearance is depicted on Fig. 1c. A close-up look at similar structures demonstrates that the masking layers are constructed by arrays of nano-fibrils (Fig. 2c) with the underlying layer showing systematic arrangement and those on top being more randomly placed. Also evident from Fig. 2d are the individual nano-fibrils of variable diameters, typical of micro-fibrillated cellulose [15]. For ranging between 1 nm to 100 nm diameter, by standard definition [16], these are classifiable as nano-fibers.

Delamination Check. CMR synergy is easier to imagine by correlating the fibrillation effects to the fibre sizes. Table 2 matches the fiber sizes with the possible different CMR effects, with each tick representing proof of observation. Related observations are presented in Fig. 3.

Table 2, Extent of Shearing Effects

Structure &Dimension	**Mechanical Refining Effects**		
	Fibrillation	**Delamination**	**Condition**
Vessel Element and vascular bundle			APMP
Macro-Fiber (>500 μm)	✓	✓	APP
Micro-Fibril; 5-100 μm	✓	✓	APFI;APP
Micro-Fibril; <1 μm	✓	✓	APFI; APP
Nano-fibril; 80-100 nm		✓	APFI
Nano-fibril; < 80 nm	✓	ND	APFI

NB: 1. segmentation, split and kink are common phenomena. 2. Macro-fibres: diameter about 1 mm | micro-fiber (EFB[18]): diameter≡8-26 μm | Fibril≡ >8 μm. 3. Nano-fibril≡1-100 nm [15],[16].

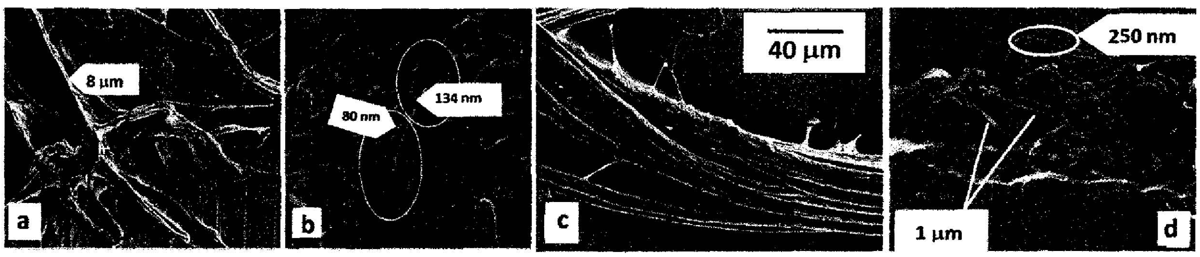

Fig. 3, Delamination effects (a) of 8 μm (diameter) fiber (b)10-134 nm fibril (c) of 25 μm fibre from the 40 μm split vascular bundle, which can be ruptured to (d) checkerboard pattern fibrils.

Fig. 3 presents the extents of delamination effects amongst fibers rooted from EFB via APP and APFI systems, respectively. Extensive delamination was achievable by multi-stage API and refining denotable as high CMR synergy (Table 1) in the APP system. The resultant structures classified as EFB fiber [17] having diameter of 8 μm (Fig. 3a) must have arisen from the peeling of TN-webs initially wound to form a larger diameter fiber. Fibers fibrillating from the 40 □m split vascular bundle (Fig. 3c), however, is also associated with APP systems, indicating partial uniformity of fibre sizes derived from the system. An extended CMR synergy offer fibrillation of the 134 nm fibril (Fig. 3b) and these are magnification of TN-webs that are more extensively delaminated fiber or the less extensively layered structure in comparison to the intact fibrous mass in Fig. 3d. The ruptured EFB microfibres showing bound layered structure of fibre webs results in the checkerboard pattern in Fig. 3d and this serves as a proof of systematic helical winding of fibrils around EFB micro-fibrils. The fact that these are still bound to the parent fibril and bound to each other as a web, indicates an incomplete removal of the recalcitrant binding materials such as modified lignin (LLF) and the skeletal silica, which, like cellulose, is also the structural strength factor to EFB.

Thus far, generation of the thin layer of nano-fibrils, is seen as occurring on several scales of fibrillar cells, depending on the applied fibrillation energies. Governed substantially by CMR synergy, the onset of delamination of the micro-fibers was detected in the APP system (Table 2). This suggests that delamination is favoured by application of multiples of 10 kWh/t to 60 kWh/t refining energy and a multi-stage alkaline peroxide impregnation stages to attain significant amount of nano-fibril webs. At x5000 magnification of the TN-webs (Fig. 3b), several of the 134 nm fibril were detected as splitting into at least 11 fibrils, suggesting the yield of approximately 12 nm diameter fibrils dangling to a parent fibre. The challenge of incomplete nano-fibrillation was also encountered in oxidative procedures such as TEMPO-assisted techniques [18-20]. In the case of APVT, the observed diminution in the fibril diameter indicates the potential of nano-fibers production from the TN-webs. Subsequent carefully controlled CMR synergy that could remove the residual fibre-cementing materials shed the light for nano-fibre production from EFB via alkaline peroxide pathway. In paper application, the presence of TN-webs in the fibre network was able to boost tensile strength by 900%. This signifies the optimism for EFB as a renewable source of nano-fiber for development of future super-strong fiber-based products. In light of rapidity and relative eco-friendliness [12], the APVT system has in intrinsic ways laid a promise for a competent and sustainable way of cascading nano-fibril network from EFB biomass.

Conclusion

Within the APVT systems, which utilize alkaline peroxide and mechanical refining, the various synergy between the applied chemical and mechanical actions witnessed a well-defined extent of EFB fibrillation: from micro fiber to the nano-fibril network. The fibrous mass liberated from the APFI and APP systems consisted of TN-webs, which improved fiber web formation by masking effects and other ensuing fiber web properties. The net feature of TN-webs also demonstrates the next target of attack by CMR synergy for cascading nano-fibers from EFB.

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Nanofibre Network Rooted from the Alkaline Peroxide Treatment of Oil Palm Empty Fruit Bunches

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Alkaline Peroxide In Synergy With Mechanical Refining As Factor In The Development Of EFB Paper Properties

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Keywords: APMP, APP, empty fruit bunch, nano-cells, paper.

Abstract. Pulp from the oil palm empty fruit bunches (EFB) was extracted via Alkaline Peroxide Pulping (APP). The pulping process was conducted through three main steps; dewaxing of EFB, impregnation of alkaline peroxide (AP) into EFB and refining of biomass to finally produce the pulp. The varying peroxide levels and number of impregnation stages were found to affect the refining energy consumption and the properties of the resultant pulp and paper. Diagnosis by electron microscopic imaging revealed a strong correlation between paper properties development and paper surface morphologies. By multiplying the stages of the low alkaline peroxide level (2:2.5% AP) impregnation, refining energy could be reduced by 30% while improving brightness and paper mechanical properties. Higher alkaline peroxide level (4:5% AP) could reduce the refining energy by 50% while still improving brightness. Beyond these AP levels (8:10% AP), refining energy could be reduced by 67% by increasing the number of impregnation stages, with positive effects on brightness and paper mechanical properties. The findings suggest that increasing the AP impregnation stages had exposed more active sites to react with AP. The enhanced AP accessibility to EFB structures facilitated mechanical fibrillation of EFB vascular bundles through the refining process. The proper synergy between AP and the adopted mechanical refining was the factor that triggered the liberation of nano-cells from EFB biomass and this had ultimately improved paper properties.

Introduction

The oil palm, *Elaeis guineensis*, is native to West Africa, but now planted in most of tropical countries all over the world. It has become the most important industrial crops especially in Malaysia and Indonesia [1-3]. Oil palm is the biggest source for edible oil and fat production, and its global demand is increasing from year to year thus, triggered the palm oil production. This would result in accumulation of palm oil biomass waste, like palm kernel, oil palm trunk, frond, and EFB.

EFB can be obtained after fruits removal in the making of crude palm oil (CPO) and is very abundant. In the past, EFB was burn in the incinerator for energy source and the rest was left on the plantation floor during replanting and pruning. Nowadays, this biomass is processed to become fertilizer for the plantation, which considered as low value-added product. EFB is high in cellulose and hemicellulose content, which are 62.9% and 28% respectively and also lower in lignin content, which is only 18.8% [4]. This potential is very attractive for the production of higher value-added product such as pulp and paper.

To obtain the EFB pulp and EFB paper, we use the alkaline peroxide pulping (APP), which is derived from the alkaline peroxide mechanical pulping (APMP™). APMP™ was first found by Andritz in 1989 [5] and it has been proven as widely applicable for either wood or nonwood resources [6-10]. Alkaline peroxide pulping as a semimechanical pulping has some beneficial features compared to chemical pulping, such as soda and kraft [11]. The features include low temperature usage, which lowers the energy used, high pulp yield in the range of 70-80%, and also high brightness of 60 to 74% ISO without bleaching [12].

However, information on alkaline peroxide pulping of EFB, such as EFB fiber responses to the alkaline peroxide treatment during the impregnation process and in correlation to handsheet properties still lacking. Without proper analysis on these responses, the maximization of chemical power cannot be done and this is likely to lead to unnecessary wastage. For this purpose, we seek for the possibility of working at extreme chemical range for maximization of chemical penetration into the biomass. The effects were observed in terms of handsheet network which responsible for the handsheet properties. Fiber bundles separation, fibrillation and fiber bonding were photo captured by SEM examination. This study was done by varying the chemical usage in the application of single and multiple stages of impregnation which affect the refining impact on the biomass.

Experimental

Preparation of Raw Material. The vascular bundles of EFB were obtained in the form of bales. These were loosened, washed thoroughly and air-dried before grinding to 500-micron particles. Dewaxing was done by soaking the biomass in distilled water at 70°C for 30 minutes for 50% extractives removal.

Alkaline Peroxide Impregnation. The alkaline peroxide (AP) was prepared by premixing hydrogen peroxide and sodium hydroxide of Merck Schuchart, Germany. AP treatment on EFB was allowed for 40 minutes at 70°C. Then, the AP-treated biomass was pressed to remove about 80% of the liquor. This was called single impregnation. For treatment involving multiple impregnations, the said process was repeated by applying fresh chemicals on AP-treated biomass after mechanical compression.

Table 1, Sample Labeling

Notation	Chemical Level (AP ratio)	NaOH (%)	H_2O_2 (%)	Impregnation stages
S-A	2:2.5%	2	2.5	Single
M-A	2:2.5%	2	2.5	Multiple
S-B	4:5%	4	5	Single
M-B	4:5%	4	5	Multiple
S-C	8:10%	8	10	Single
M-C	8:10%	8	10	Multiple

Refining Process and Making of Handsheet. Refining process was conducted by using the Sprout Bauer Refiner to allow fibrillation. The pulps obtained were made into handsheets in accordance to TAPPI Test Methods 1997 [13].

Mechanical and Optical Testing. The mechanical tests conducted in this study were folding endurance, burst, tensile and tear resistance in TAPPI 227 and zero span strength in TAPPI 231. Meanwhile, the optical properties included brightness and opacity of paper (TAPPI 425).

Scanning Electron Micrograph (SEM). The handsheet surfaces were observed by using Leo Supra, 50 VP, Carl Zeiss Scanning Electron Micrograph. The samples were placed on a stub using double-sided electrically conducting carbon adhesive tapes and then gold coated using Polaron Equipment Limited model E500 with a voltage of 1.2kV and 20Pa for 10 minutes.

Results and Discussion

APP is a type of pulping method that consist of three main processes, dewaxing, impregnating and refining. Dewaxing primarily refers to the removal of the extractives, which mainly present in the primary wall of fibers. Alkaline peroxide impregnation is therefore responsible for further release of extractives including minerals such as calcium and the transition metals such as manganese, copper, iron and zinc. Moreover, chromophoric compound removals and modification of lignin by the perhydroxyl groups occurring at 70°C. This resulted in the brightening of fibers in addition to pre-splitting of EFB vascular bundles and pre-access of AP for softening which assisted subsequent refining process.

The level of alkaline peroxide used and the number of impregnation stages could be adjusted to achieve the desired properties of the resulting pulp, but refining also plays an important role towards the completion of pulping process. Refining would promote fiber fibrillation, fiber flexibility and bonding power. The shearing effects caused the primary fiber wall to be removed and also promoted fiber swelling. This would result in paper with good conformability and better fiber network. Different AP treatment would affect refining impact and thus, affect paper properties.

The effects of variation in APP treatment on pulp and paper properties together with refining energy consumption denoted by Specific Refining Energy (SRE) are described in Table 2. Paper strengths (tensile, tear, burst, zero span and folding endurance) generally increase as the increase of impregnation stages at each chemical level. The SRE is reduced with the increase of total chemical used. This is because the reduction in lignin content reduces the stiffness of the fiber and subsequently reduces the required refining energy. Reduction in lignin also increases the brightness and reduces the Light Scattering Coefficient (LSC) as the handsheet become smoother.

Table 2, Properties of EFB-APP Pulp and Paper Produced

Properties	S - A	M - A	S - B	M - B	S - C	M - C
SRE (kWh/ton)	30.92	21.66	NA	15.54	NA	10.14
Tensile index (Nm/g)	6.4±0.7	14.9±1.3	16.1±1.2*	18.1±1.6	16.9±0.9*	25.3±2.4
Tear index (mN.m^2/g)	3.3±0.1	4.6±0.2	4.9±0.4*	4.8±0.2*	4.9±0.3*	6.1±0.3
Burst index (Kpa.m^2/g)	0.9±0.0	0.9±0.1	1.0±0.1*	1.0±0.1*	1.0±0.1*	2.1±0.1
Zero span index (Nm/g)	42.8±6.3	56.6±3.5	49.0±5.6	58.7±4.2	55.6±5.4*	71.6±3.9
Folding endurance (no. of double folds)	2.1±0.4	14.3± 2.8	18.3±5.6*	29.1± 12.8	25.7±8.0*	251.6± 132.0
Brightness (%ISO)	60.3±0.4	66.5±0.6	67.7±0.3*	71.5±0.4	64.8±0.2	73.2±0.8
Tappi opacity (%ISO)	90.8±0.6	86.9±0.6	87.0±0.7	86.3±0.6	87.9±0.7	85.8±0.5
Print opacity (%ISO)	85.2±0.9	77.9±0.8	78.0±1.0	75.9±0.8	80.1±0.9	74.5±0.7
LSC (m^2/kg)	31.2	26.7	27.1	26.7	27.5	25.9

* The change is insignificant.

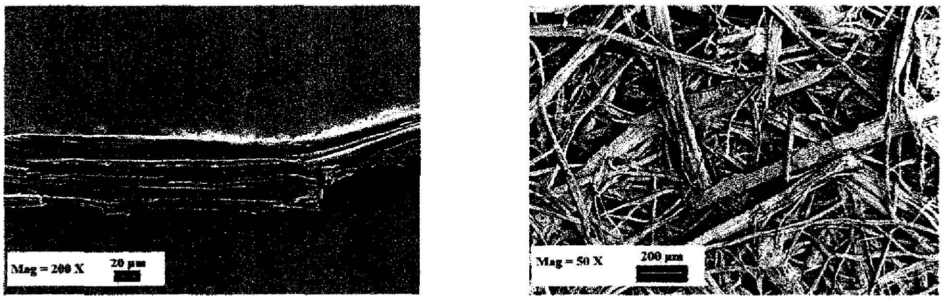
The role of AP with mild experimental temperature is more effective in destroying chromophoric groups responsible than removing lignin from the EFB structure [14]. Subsequent impregnations is believed would allowed more access of AP into the fiber strands, hence, allowing more handy reaction between AP and active sites of EFB. The synergistic effect between AP and mechanical pressing would generate numerous macro and micro ruptures. Thus, for the subsequent impregnation stage, the new available space allowed more occupation for active AP, which in turn triggered removal of more components from EFB. Thus, fiber bundles become softer while refining stage cause further liberation of silica bodies, fiber splitting and fiber fibrillation, which finally affect lignin quantity. Therefore, increasing the chemical power in synergy with mechanical actions in APP treatment could have separated lignin chain from EFB chemically and physically.

SEM revealed the factors behind the sheet strength and refining energy consumption. For examples, SEM on fibers and sheet networks produced by multiple impregnations at different chemical levels in comparison with single-stage impregnated pulp by 2:2.5% AP (A) which represents low sheet strength were observed. Fig. 1 shows predominance of vascular bundle, as a consequence of poor fibrillation due to low accessibility of chemicals by S-A. The predominance of fibre bundles implies that high stiffness of the biomass is caused by the presence of lignin, which also has prevented the cell wall from detaching and prevented fibrillation. This resulted in low sheet strength of the paper produced.

In the multiple impregnation of 2:2.5% AP (M-A), part of the fibrous mass appeared as completely split into individual fiber, while some are partially split. The reduction in vascular bundles has improved the fiber bonding by improving fiber fibrillation. According to paper properties and examination by SEM (Fig. 2), extending chemical penetration by M-A is likely to cause:

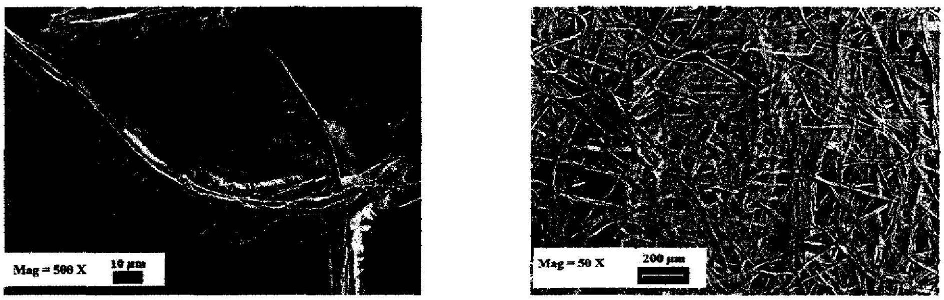
- Soften fiber bundle, easy fiber separation during refining
- Higher number of fibrils are generated, results in higher bonding ability and higher mechanical properties
- Refining impact exposes lumen area of fiber, but the coarseness of the fiber is still apparent.
- Higher brightness due to high chromophoric groups removed.

With an increase in chemical level to 4:5% AP, paper surface formed by multiple impregnations show a flattened form of fibre bundles and an increase in fibrillation especially at the end of the fibers (Fig. 3) which improves the handsheet strength.



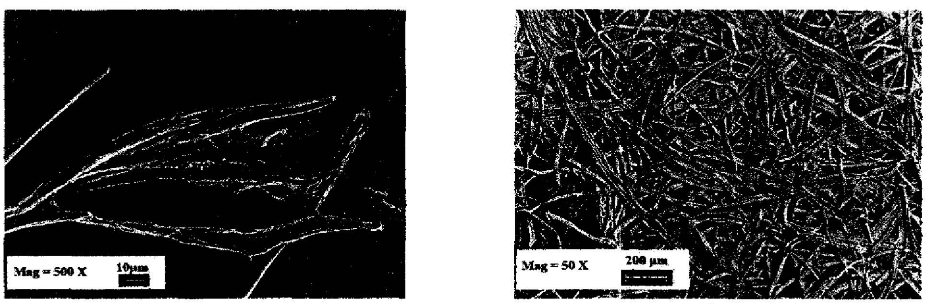
(a) (b)

Fig. 1, SEM on fiber bundle (a) and handsheet surface area (b) made by S-A.



(a) (b)

Fig. 2, SEM on fiber (a) and handsheet surface area (b) made by M-A.



(a) (b)

Fig. 3, SEM on fiber (a) and handsheet surface area (b) made by M-B.

By further increasing the AP chemical level to 8:10% AP, there is high improvement on fiber bonding and on handsheet surface. Examination of 8:10% AP handsheet strength also shows favourability to M - C compared to both pulp M - A and M - B. The tensile strength of a handsheet is quite sensitive to the change in number of fiber bonding. The increment of AP level from 4:5% to 8:10% by multiple impregnations has increased the tensile index by 40% as seen in Table 2. The effect of extending chemical penetration by M - C shows favourability in softening the lignin structure, which results in the conversion of most fiber bundles into well fibrillated individual fibers (see Fig. 4(a)). M-C is also likely to promote fiber splitting while maintaining the fiber strength as evidence by high tear strength (Table 2) that arises from good fiber bonding without shortening effects. This is clearly shown by the SEM on M – C paper network in Fig. 4(b).

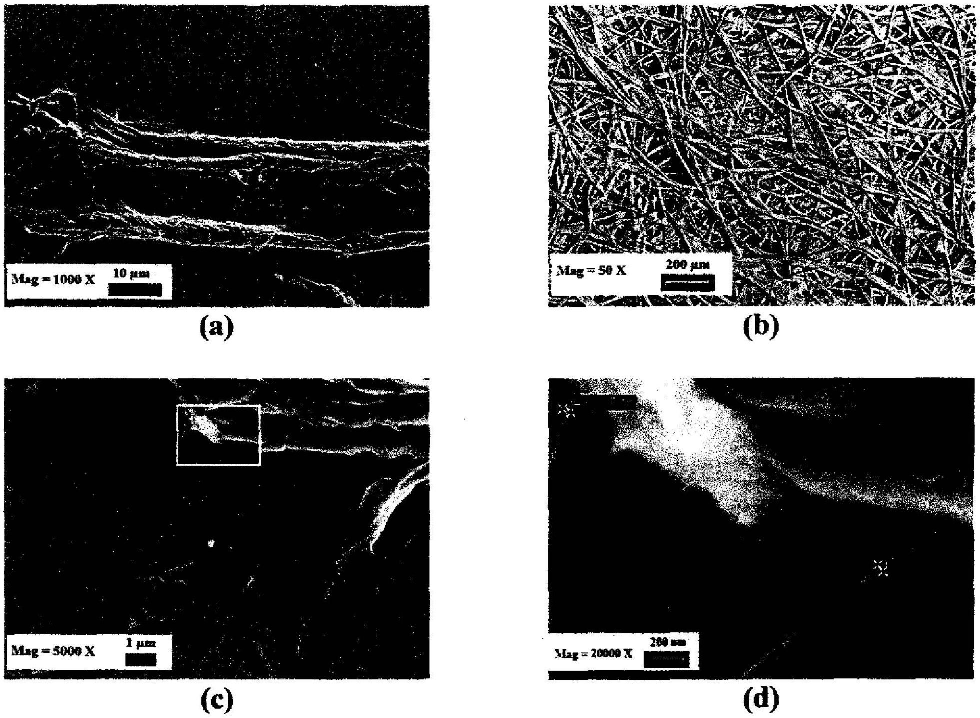


Fig. 4, SEM on fiber (a), handsheet surface area (b), fibrillated parts (c), nano-fibrils (d) made by M-C.

M-C rendered improvement in the fiber network. Fibre bundles are no longer found. Fibers were well bound due to excellent collapsibility and this has created good fiber network (Fig.4(a)). Surface of the associated sheet also revealed 'fiber coalescence' (Fig.4(b)). In synergy with the residual chemical from multiple impregnations, the shearing effect by refining process had intensively peeled the cell wall layers of the fibers. The synergistic effect cause delamination of the S2 layers, which results in unraveling nanofibrils network evident from thin webs of nano-fibrils shown in Fig. 4 (c) and Fig. 4 (d).

It is apparent that the increase of chemical penetration results in a more softened lignin macromolecule and has improved the refiner impact on the biomass. Shearing action during refining would cause delamination of fiber cell walls and this enhanced fiber swelling capacity and in turn promoted internal fibrillation. The outcome is higher fiber collapsibility, which would form ribbon like elements of great conformability as previously shown in Fig. 4. If untangled, these structures would help bind adjacent fibers, hence increasing the bonding sites and mechanical strength of paper. An increased number of impregnation stages had also promoted external fibrillation (as proven by SEM on fibers) which leads to the increase of inter-fiber bonding. Therefore, the applied impregnation stages had improved the said tensile, folding, tear and burst strengths of the produced papers as summarized by Table 2.

Conclusion

Extending the effect of alkaline peroxide in synergy with mechanical action increases the amount of nano-fibrils network responsible for fiber bonding and the resulted paper properties development. Improving the synergy is the prominent gateway to uncover the possibility of generating valuable nano-fibril cells.

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Alkaline Peroxide in Synergy with Mechanical Refining as Factor in the Development of EFB Paper Properties
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SILICA OF THE OIL PALM EMPTY FRUIT BUNCHES – AN INFINITE AMAZEMENT

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The abundance of silica in plants is to fit many purposes. In the oil palm empty fruit bunches that was initially intended for extraction of paper making fibers, silica bodies were found to range between 10-20 □m and these were effectively removed by mechanical impacts. Removal of silica was also aided by the subsequent chelation with DTPA and this provides evidence of the adjacent localisation of the mineral to the silica bodies. Despite removing 86% of the microbodies, the treated biomass revealed the presence of 0.3% (Wt/Wt residual silica. Scanning electron microscopy of the ash of the EFB cellulose mass unveiled the presence of siliceous thread amidst the common microbodies. SEM examination of the alpha-cellulose and the EFB pulp ash presents evidence of siliceous fluid transport structures believed to be part of the skeletal silica in the palm fruit bunch structure. The smorgasbord shapes and sizes of the found siliceous structures reflect nature's amazing craftsmanship of living things for serving such specific functions as mechanical, aesthetical, defence and infinite other purposes.

Keywords: EFB; pulp; paper; oil palm biomass; silica, SEM.

INTRODUCTION

Elaise guineensis, the cash crop that avails Malaysia as world's second largest palm oil producer [1], generates 17 million tonnes of empty fruit bunch (EFB) residue [2]. With product LCA clinging to the knowledge of waste management system, ideas of products' end-of-life are aligned to recycling and reusing possibility. With the aforesaid phenomenon, EFB, the once accumulating waste, has become today's commodity. This is especially enlivened with the blooming of pulping, papermaking and bioenergy sectors where cellulosic biomass is in great demand [3]. Apart from being the precursor in pulping, papermaking [3-5], biofuel production [3, 6], panel product fabrication and cleansing of water bodies [7], the high mineral contents of EFB has given it strong credit for use as glazing materials [8].

Although the EFB industrial application has by now been proven feasible, minerals residing the biomass may become a major source of problem in applications where organic mass is favoured in solo. The transition metals, for instance, are known to cause colour reversion of certain high-brightness products like paper. Apparently, this is the typical tribute of copper, iron and manganese [9], also commonly reported to cause uncontrolled peroxide consumption [10].

One other member in the controversial family of mineral is the opal of plants, known scientifically as silica. 0.3% of these abrasive materials could hamper process efficiency [11] due to wearing and thus, the need for periodic replacement of cutting tool. The propensity of silica to dissolve in alkaline reaction system, in addition, results in thickening of black liquor (when pulping in concerned), which in turn, poses a problem in the chemical recovery process [12, 13]. Furthermore, when present in paper-base endproducts, silica could cause abrasion of such gadgetry as knives, dies, punch, typewriter [14] or printer head and causes micro-scratch on sensitive surfaces. Meanwhile, silica occupying its craters in intact biomass could prevent penetration of chemical [5] exactly the way pathogenic invasion is prevented [6].

In biological systems such as plant, silica bears specialized functions and never existed in elemental form [7]. The smorgasbord nature of the studied siliceous structures of EFB is hereby mapped to the rationale of their existence. This was achieved by zooming into the native and the treated microstructures using SEM as a tool for marveling at nature.

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biomass, despite the presence of the residual silica bodies and the less abrasive silica skeletons.

The studied sequential mechanical and chemical treatments of EFB (as well as the underlying science), also allow better understanding of the concept of creation versus the assigned function. This is even relevant to such fine materials as the micro-elements in the universe. The nature of atomic stoichiometry and affinity for other minerals is the deliberately designed nature to serve the defined function. From the angel of creations' behaviour, all these are indications of loyal submission to the Creator or Commander, in line with an indigenous saying: *not for naught have We created you..* (23:115) and that *"I have only created Jinns and men, that they may serve Me.* (51:56) [20].

Silica and the laid evidence of its functions are the less apparent signs when comparing to the huge and apparent natural behavior like alternation of night and day (2:190)[20], the sailing of ships on the water (2:164, 14:32)[20], the orbiting of the sun and the moon (21:33)[20] that science explained as the effect of gyration and inertia, the standing firm of mountain (21:31, 16:15) [20] and the sky as a station that exist without pillars (31:10) [20]. The witnessed amazing creation and amazing submission or obedience are reflections of the perfect craftsmanship of the All-knowing, the Governor, the Creator who is simultaneously the Commander who has complete knowledge of all living things(6:101-103)[20]. These are the natural phenomena that are visible and unveiled through contemplation as also guided by the indigenous saying: *..in the creation of the heavens and the earth and the alternation of night and day there is indeed Signs for men of understanding (man who contemplate)* (3:190). For such micro-elements as silica, the path to marvel at the science behind nature is particularly made feasible by scanning electron microscopy as tool for analysis.

CONCLUSION

Silica, forming EFB micro-component serves amazing functions visualised with the aid of SEM imaging of EFB and EFB-derivative ashes following bizarre desilication outcome achieved by treatment of EFB with DTPA. The smorgasbord shapes of the siliceous structures, whether spiky granular bodies or sculptured into the biomass structure, are evidently the match between design and function laid in the concept of purposeful creation. The undertaken functions that are regarded as true submission to the divine commands, reflects the an amazing craftsmanship of nature that is hardly realised without such superb imaging technique as SEM. The many correlations between the results of analysis and contents of indigenous knowledge forge an infinitely amazing connection between components of nature and the specificity of their functions.

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SCANNING ELECTRON MICROSCOPY FOR IDENTIFICATION OF PAPER STRENGTH DEVELOPMENT BY TWO VARIATIONS OF REFINER PLATE PATTERN

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The abundant oil palm Empty Fruit Bunch (EFB) was used as raw material in the low-cost, low environmental impact Alkaline Peroxide Pulping (APP) to produce pulp and paper. Pulping was performed by using two types of refiner plate pattern, 12716 and D2A505. For each plate pattern, samples were prepared by treatment with 2:2.5% (wt/wt) alkali-to-peroxide (AP) ratio applying different number of AP impregnation stages. For plate 12716, the resultant papers show tensile strength varying from 6.9 Nm/g to 16.22 Nm/g, tear strength varying from 3.6 mN·m²/g to 5.2 mN·m²/g and folding endurance varying from 2 to 25. As of plate D2A505, tensile strength of papers made from the produced pulp range from 6.93 Nm/g to 29.77 Nm/g, tear strength from 2.9 mN·m²/g to 5.34 mN·m²/g, and folding endurance from 2 to 1633. Examination of paper surface by Scanning Electron Micrograph (SEM) revealed an increase in the extent of what appeared under SEM as 'fibre coalescence', implying extensive overlapping and bonding between the produced pulp mass. For all sets of lower strength pulp network, the produced fibrous mass was predominantly fibre bundles without any sign of coalescence. SEM analysis also witnessed the presence of long individual fibres and fibre bundles having correlation with paper resistance to burst and folding. The established correlations demonstrate the important way scanning electron microscopic technique serve for comprehensive understanding of fibre and fibre bonding characters in paper quality assessment.

Keywords: alkaline peroxide pulping; APMP; EFB; impregnation; paper properties, SEM

INTRODUCTION

The oil palm empty fruit bunch (EFB) is an all-year abundant biomass generated from palm oil extraction from the species of *Elaise guineensis*. Introduced as an ornamental plant of West Africa, *E. guineensis* was first brought to Indonesia in 1848 and to Malaya in 1911 [1]. As today's cash crop, the oil palm gradually contribute to the major revenue of the countries, placing them as world leading producer of palm oil and, of course, the major generator of EFB.

In the effort of utilizing this cellulosic biomass and prevent its accumulation, the concept of APMP [2-6] was mimicked and applied, initialising it as Alkaline Peroxide Pulping (APP). The properties of the produced pulp were studied and the surface morphology of the pulp network was examined. Scanning Electron Microscopic (SEM) analysis of the pulp network was seen as an effective tool for understanding fibre bonding and strength development. This paper reports the properties of APP pulp from EFB. The outcome of SEM analyses of the papers corresponding to the pulp produced by increasing the stages of alkaline peroxide (AP) impregnation and by refining with two variations of refiner plate patterns are hereby discussed.

MATERIALS AND METHODS

Preparation of Raw Material

The vascular bundles of EFB were obtained in the form of bales. These were loosened, washed thoroughly and air-dried before grinding to 500-micron particles. Dewaxing was done by soaking the biomass particles in distilled water at 70°C for 30 minutes and this was to achieve 50% removal of the extractives components.

Alkaline Peroxide Impregnation

The alkaline peroxide (AP) was prepared by premixing hydrogen peroxide and sodium hydroxide. Reaction with 2:2.5% alkaline peroxide was allowed to stand for 40 minutes at 70°C before pressing the biomass to 20% residual moisture. This process is denoted as 1-stage impregnation while for treatment involving x times repetition of the said steps is denoted as x-stage impregnation. Repetition (x), however, was no more than four times and each time involves the application of fresh chemicals on the biomass.

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CONCLUSION

SEM results offered important information on hand sheets morphology and described fibre bonding behaviours. These make SEM a useful aid in identification of pulp properties development. In this regard, refiner plate pattern was profound in its effect on pulp and this is particularly true for multiple-stage alkaline peroxide impregnation.The targeted pulp properties can be developed by varying the refiner plate patterns and AP impregnation stages. For certain applications demanding for high strength and flexibility, refiner plate pattern D2A505 would serve the purpose.

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WASTE MANAGEMENT AND CONTROL TECHNOLOGY

...ATION OF PAPER STRENGTH DEVELOPMENT BY TWO VARIATIONS OF REFINER PLATE PATTERN

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...ACT

... Empty Fruit Bunch (EFB) was subjected to low-cost, low environmental impact Alkaline Peroxide ... (APP) to produce pulp and paper. Pulping was performed by using two types of refiner plate pattern, ... and D2A505. For each plate pattern, samples were prepared by treatment with 2:2.5% alkali-to-peroxide ... applying different number of AP impregnation stages. For plate 12716, the resultant papers show ... strength varying from 6.9 Nm/g to 16.22 Nm/g, tear strength varying from 3.6 mN•m²/g to 5.2 mN•m²/g ... endurance varying from 2 to 25. As of plate D2A505, tensile strength of papers made from the ... pulp range from 6.93 Nm/g to 29.77 Nm/g, tear strength from 2.9 mN•m²/g to 5.34 mN•m²/g, and ... endurance from 2 to 1633. Microscopic analysis of paper surface morphology revealed an increase in the ... of 'fibre coalescence', implying extensive overlapping and bonding between the produced pulps. For all ... lower strength pulp network, the produced fibrous mass was predominantly fibre bundles without any sign ...escence. SEM analysis also witnessed correlation between the presence of long individual fibres and fibre ... having correlation with paper resistance to burst and folding. The findings established correlations ... paper surface morphology and the nature and extent of fibre-to-fiber bonding in paper strength ...ment.

...words: APMP, alkaline peroxide pulping, EFB, impregnation, paper properties.

...CTION

... ...ability of oil palm empty fruit bunch (EFB) and its all year availability has increased the interest of using this ... residue in pulp and papermaking [1-3]. In Malaysia only, there are almost 4.98 million hectares of palm oil ... area in 2011 [4]. This planting area could produce almost 90 million tonnes of oil palm fresh fruit bunch (FFB), ...-22% contains EFB [4, 5]. Of these, 19.3 million tonnes of EFB remain unused [6]. This large quantity of ...osic biomass need to be treated properly and utilized, rather than being burned in incinerators or left on the ... floor of palm oil mills and causing great environmental problems [7,8].

... this purpose, Alkaline Peroxide Pulping (APP) developed by the beneficial principles credited to Alkaline Peroxide ... Pulping, APMP™ can possibly be adopted. This paper reports the development of paper strength by increasing ... of AP impregnation and varying refiner plate patterns. The correlation between paper properties and the unique ...gical features witnessed by SEM is hereby discussed.

...OD

...ation of Raw Material

The vascular bundles of EFB were obtained in the form of bales. These were loosened, washed thoroughly and air-dried ... grinding to 500-micron particles. Dewaxing was done by soaking the biomass particles in distilled water at 70°C for 30 ... for removal of 50% of extractive components.

...ine Peroxide Impregnation

The alkaline peroxide (AP) was prepared by premixing hydrogen peroxide and sodium hydroxide. Reaction by 2:2.5% ... peroxide was allowed for 40 minutes at 70°C and then pressed to remove about 80% of the liquor. This was called 1-... impregnation. For treatment involved 2-stages or more impregnations, the said process was repeated by applying fresh ...icals on the biomass.

... PAPER MORPHOLOGY AND MECHANICAL PROPERTIES WITH EXTENDED BEATING OF EFB PULP

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...ACT

... from the alkaline peroxide pulping (APP) of EFB was beaten from 500 revolutions to 10 000 ... using PFI mill to investigate the morphological changes undergone by the pulp and the resultant ... paper sheet properties. As a result of beating, pulp elements were observed as intensely fibrillated, ... the amounts of fibre bundles and thus, slandering the interruption in the inter-fiber bonding. To a ... extent, beating was also seen as unwinding the structure of vessel element to a single strand of loose ... body. These fibrillated vessel elements of APP pulp from EFB plus the fines element germinating from ... segmentation of the vessels, were the factors contributing to the overall strength improvement of the ... EFB pulp network. The applied increment in beating revolution had apparently widened the known ... spectrum quality of APP pulp from EFB. This reveals promise for EFB for application in specialty paper ...

...ds: APP, Beating, EFB, fines.

...CTION

... dross of palm oil milling activities, oil palm empty fruit bunches (EFB), has enticed world-wide interest for ... as raw material in sustainable product development. In tandem with Malaysia's long history of good ... practices pertaining waste management, effluent management and zero-burning [1] today, research on ... of the sheer 19.3 million tonnes of EFB continues to grow. EFB can be minimally processed to suit application as ... sorbents [2-4]. It is also a type of biomass currently researched for the practical possibility of biofuel production, ... the often-said snags. Beyond research, today, a small amount of EFB is used as medium-density fibreboard, mats, ... cushions and light furnitures. It is also compressed as briquettes and incinerated for electricity generation [5]. ... destruction of EFB lignocellulose matrix allows production of siliceous melt enabling glazing of ceramics and ... On the contrasting consideration, EFB, having predominance of cellulose, lower level of lignin in comparison to ... wood and having unique fibre characteristics, render the residue more viability as raw material for pulping and ... to paper-based products [7-9] as compared to bioenergy [9] and glazing applications.

... pulp productivity perspective, per hectare palm oil plantation could generate EFB pulp at least double the per ... pulp harvested from the local rainforest. This corresponds to over 88 million trees-saving, on the assumption that all ... could be converted to pulp [5]. An economic way of doing this was attempted by applying an environmentally benign ... process concept of the alkaline peroxide mechanical pulping, APMP. Being sulfur and chlorine free, the technique ... pulping and bleaching in a single process, thus, eliminating the need for a separate bleach plant and the ensuing ... and maintenance costs. Apart from the acclaimed [10-13] simplicity, various possible adjustments that can be made ... refining parameters, such as alkaline peroxide level, stages, temperature of the alkaline peroxide and etcetera, to suit to ... of biomass and the resultant pulp quality. The process flexibility and high adaptability to a wide spectrum of ... were first demonstrated by Cort and Bohn [14] based on the success of APMP™ of aspen wood. Subsequent works ... successful application of the system to different wood species such as birch, maple, and poplar [15, 16]. Through ... upgrading measures, Xu and co-workers reported success of adapting a modified APMP system [17] to various non-... species, for instance kenaf, straw, baggase, and jute [11-13], as well as to selected tropical hardwood such as acacia ... [18].

Early attempts of adapting APMP to EFB [6, 7, 19] observed the wide possibility of pulp quality by adjustments of ...mental parameter and machinery. The effects of beating the APP pulp derived from EFB, which also offers a huge ... in pulp and paper properties are hereby discuss the outcome of subjecting the produced APP pulp to the varying

AUGMENTATION OF ALKALINE PEROXIDE PULP NETWORK BY CO-GENERATED FILLER

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ABSTRACT

Desirable and eco-friendly pulp-based product properties are governed by factors like choice and suitability of raw material, the design and operation of pulping process and choice of additives. Fines co-generated at the refining stage during an alkaline peroxide pulping of oil palm empty fruit bunches (EFB) were collected based on their passage and retention capacities when subjected to varying mesh-sizes stainless-steel square mesh wires. Analysis shows that blending 12% of the 400-mesh fines (P300/R400) with the normal 200-mesh pulp fraction enhanced paper tensile strength by 100% due to their favourable dimensions. This defines the usefulness of fibrillar particles whose cell wall collapsibility increases the web density by increasing bonding ability and thus, strength of pulp-based products such as paper and other moulded products. The study demonstrates fines functioning as natural filler for augmentation of pulp network. The introduced recovery and utilization of the refining discharge elements was found to reduce 70% turbidity and this improvement will help reduce the costs pertinent to generation of whitewater in the pulping system.

Keywords: Empty fruit bunch (EFB), fines, refining, vessel element.

INTRODUCTION

Global resources consumption for 2010 reveals a persistent dependency on wood as a natural resource for pulping and papermaking, and this intensifies concerns over world carbon emission from deforestation. To gradually reduce the 70%-to-30% portion of wood-to-nonwood fibre supply, pulp and paper consumption patterns need to be revisited [1]. Adaptation of existing technology and innovation of technology for pulping and processing of non-woody materials, which can be extra demanding in comparison to wood pulping [2], also needs extensive research and proper documentation. Renewed interest in non-wood utilization research activities need proper monitoring and redirecting to ensure adherence to sustainability strategies such as cradle-to-cradle and cradle-to-gate product life cycle as well as zero-waste systems. These efforts point to waste minimisation and benign carbon accounting results.

Asia is an influential source of non-wood pulp from annual fiber crop, agricultural residue (or agro-waste) and non-plant fibrous mass such as algae, rags and animal waste. In the course of palm oil milling in Malaysia, for instance, 19.3 million tonnes of EFB is generated each year as the palms are pruned for oil extraction [3]. Traditionally, the EFB are left to rot in the environment or burnt in open air, which creates tremendous environmental concern. While open burning pumps in carbon dioxide into the atmosphere (an excess of which can lead to global warming), leaving the residual fruit bunch to rot in the environment attracts pests, besides being a source of foul odour. Utilisation of the industrial-cum-agricultural residue, therefore, offers productive management of the waste from the country's major cash crop. From pulp productivity perspective, per hectare palm oil plantation could generate EFB pulp at least double the per annum pulp harvested from the local rainforest. This corresponds to over 88 million trees-saving, on the assumption that all EFB could be converted to pulp

To date, research on utilization of EFB continues to grow. EFB can be minimally processed to suit application as pollutant sorbents [4, 5, 6]. It is also a type of biomass currently researched for the practical possibility of biofuel production, despite the often-said snags. Beyond research, today a small amount of EFB is used as medium-density fibreboard, mats, mattresses, cushions and light furnitures. It is also compressed as briquettes and incinerated for electricity generation [3]. Similarly, destruction of EFB lignocellulose matrix allows production of melt siliceous glaze by high temperature incineration of the biomass. This has enticed creative application such as glazing of ceramics and pottery [7], for interior decoration application. On the contrasting consideration, EFB, having predominance of cellulose, lower lignin in comparison to most local wood and having unique fibre characteristics, render the residue more viability as raw material for pulping and conversion to paper-based products [8, 9, 10] as compared to bioenergy [10] and glazing applications.

SURFACE MORPHOLOGY OF PAPERS FROM OIL PALM EFB ALKALINE PEROXIDE PULP

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ABSTRACT

The surface of papers made from alkaline peroxide pulp of oil palm empty fruit bunch (EFB) was examined using scanning electron microscope. Strength properties of handsheets correlate proportionally with fibre coverage and masking of fibers on paper surface. This is closely associated with pulp mass characteristics such as the extent of fibrillation and cutting of fiber elements as well as the extent of fibrillation and segmentation of vessel elements, which govern the effective inter-fiber bonding of the pulp network. This is also associated with fiber collapsibility and flexibility, reflected upon such mechanical properties as tensile, tear and burst indices, etcetera. Fiber characters and paper properties, in turn, is substantially affected by EFB responses to the principal pulping chemical, alkaline peroxide (AP), applied during pre-treatment and refining stages, found most effectively applied at 4.5% AP level and 2-stage impregnation.

Keywords: APP, EFB, fiber bonding, fiber cell wall, fibrillation.

INTRODUCTION

The oil palm empty fruit bunch (EFB), the all-year abundant biomass derived from the plantation of *Elaise guineensis* is, primarily planted for oil production. This species is an ornamental plant of West Africa that first brought to Indonesia in 1848 and to Malaya in 1911 [1]. The global demand of edible oil has been increasing with an increase in world population. To date, palm oil is the biggest source for edible oil and fat production. This has triggered the growth of oil palm plantation, especially in Malaysia as one of world's largest palm oil producer. As a result of oil milling, an accumulating fibrous mass biomass waste such as EFB, palm kernel, fronds and trunks are co-generated. EFB is a fibrous material and can also be called as lignocellulosic material because it is mainly composed of cellulose, lignin, and extractives. High content of cellulose and hemicellulose in EFB [2, 3] has extended the list of non-woody materials of great potential in papermaking application.

Paper properties depend on the chemical and physical nature of the fibers when they are formed into the sheet of paper [4]. EFB constituents, which can be considered as factors affect paper properties are cellulose, hemicellulose, lignin, extractives and inorganic material such as silica. Cellulose, which is composed of only glucose, determines the character of the fiber and also a very important parameter in selecting raw material for papermaking [5]. In a study by Perez et al. [6] it was found that hemicellulose as additive is better than hemicellulose as content in fiber. Among the hemicellulose, xylans are one of the most abundant biopolymers after cellulose and may constitute more than 30% of a plant cell wall in dry weight [7]. Lignin is an amorphous and highly polymerized substance which form the middle lamella that cements the fiber together [5]. Lignin is physically linked with cellulose, as well as physically and chemically linked to hemicellulose [8]. Lignin content in EFB is quite similar to common hardwood such as Aspen [2]. The best balance of papermaking properties occurs when most of the lignin is removed from the fibers while retaining substantial amounts of hemicellulose. Extractives are found on the primary wall of fibers. Removal of extractives would promote the external fibrillation of fibers, and at the same time, it will allow hemicellulose to migrate from the inner layer to the surface layer of the fiber. The presence of silica could complicate pulping of EFB biomass. Silica is found in great number on EFB in the form of silica bodies [2].

In this experiment, the concept of APMP was mimicked and applied, initialising it as Alkaline Peroxide Pulping (APP). Alkaline peroxide brightening of mechanical pulps has been proven most effective and practical for the pulping industry [9-10]. With hydrogen peroxide, most softwood mechanical pulps can be brightened to 75% ISO brightness or higher, while hardwood mechanical pulps may be brightened as high as 89% ISO [3]. For a non-wood resource such as EFB, the information regarding alkaline peroxide treatments are still limited. There are several studies have been reported in the improvement of hand sheet properties in order to develop better operating condition of APP of EFB [3, 11-14]. However, no attempt has been done in understanding the association between hand sheet morphology of APP of EFB and the resulting handsheet properties in correlation with alkaline peroxide treatment. Physical and chemical structure of fibers can be changed

INFLUENCE OF ALKALINE PEROXIDE TREATMENT TIME ON EFB PAPER PR

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ABSTRACT

The outcome of applying APMP concept to the oil palm empty fruit bunch or EFB, the by-prod milling activity, was investigated. Prior to the simulated pulping process, denoted as alkaline APP in this study, the EFB biomass was processed for cleaning and dewaxing purposes to suit making needs. In the effort of maximizing the alkaline peroxide chemical, EFB was treated with alkaline peroxide of 2.5 % hydrogen peroxide and 2.0 % of sodium hydroxide. Reaction betw chemicals and the biomass was allowed at varying time with a standing temperature of 70^{0}C and of 10-to-1 liquor-to-EFB ratio. When the biomass was refined and made into hand sheet, the re paper properties and treatment time was revealed. It turned out that such paper properties as tensile and burst indices including brightness (% ISO) were generally enhanced with treatment t exhibited by the EFB undergoing 30 to 40 minutes treatment time at the aforementioned condi the vicinity of the optimal treatment time, penetration of the alkaline peroxide chemicals into sufficiently and this had softened the biomass enough for the subsequent refining process that making fibres. As a result, inter-fibre bonding was enhanced, which in turn improved the mech properties of the paper. It is noteworthy that the correlation between bonding enhancement and was verified using scanning electron microscopic (SEM) analysis of the fibre network, viewed fr

Keywords: APMP, brightness, EFB, mechanical properties, SEM.

INTRODUCTION

The palm oil milling sector in Malaysia generates millions of metric tonne of oil palm empty fruit bunch (EFB), oil palm fronds (OPF) and oil palm trunks (OPT), annually. Acco (2007), 36 million tonnes (odmt) of these wastes came from the empty fruit bunch (EFB) processed further to dry vascular bundles and packed to bales for storage and transportation (So

Valuable fibres attained from EFB are presently used for developing value-added prod composite product, medium density fibreboard (MDF) and fibreboard. Owing to its lower lignin OPF and OPT, high cellulose content, moderate level of extractives and moderate level of starch most suitable raw material for pulping and paper making, as compared to the other two oil palm and OPF. Besides reducing environmental impacts from waste accumulation, EFB utilization can also help Malaysia to be independent of imported fibre (Ghazali et al., 2006). One way of is by adapting the significant aspects of APMP concept of pulping to the raw material.

APMP is a process which combines bleaching and pulping in one process with alkali main driving agent. This process was foremost introduced by Andritz Sprout-Bauer, United St been recognized as today's most efficient chemi-mechanical pulping technique for hardwood. T had gained worldwide research and industrial interests due to its outstanding features like bei friendly in comparison to other pre or post conventional bleaching of pulp, which makes use of chlorine-based bleaching agents (Ghazali et al., 2006). Furthermore, APMP is proven cost elimination of a separate bleach plant which, in turn, helps the industry in reducing installation co 1991). In addition, APMP is also very flexible and can be adaptable to a variety of biomass i wood materials as bagasse, kenaf, jute and straw.

Despite its excellent features, APMP is still not operationally adopted in the Malaysia industry due to the need to thoroughly study the process quality and cost. For this reason, m investigations are underway in order to understand the process comprehensively. As one in the list of this study is to examine the effect of treatment time on the properties of alkaline peroxide pulp is hereby presented.

e of biomass), 30 minutes to 40 minutes appeared to be the time for maximum of these brightening EFB. The irreversibility of the brightening effect is also apparent from the APMP paper exposed to re than one year and this will be discussed at length in a different publication.

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ptimality of 30 to 40 minutes for adequate reaction between EFB and alkaline peroxide was deducible ts of this study. Absolute consistency was depicted on the mechanical properties (folding endurance, and tensile index) and optical properties (brightness) as well as morphology study of the resultant Results demonstrated the important influence of alkaline peroxide treatment time to effect both EFB and softening of the biomass to lubricate the subsequent refining process. Thus, at the said time, res and fibrillae offered excellent paper formation.

GMENTS

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